

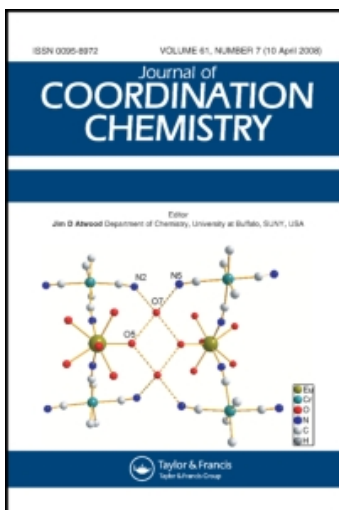
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Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title-content=t713455674>

Reactivity studies of (⁶-arene)ruthenium(II) dimers with arylazoimidazole ligands: molecular structure of [(⁶-p-cymene)RuCl(Me-C₆H₄-Nequals;N-C₃H₂N₂-1-CH₃)]PF₆

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Online Publication Date: 01 January 2007

To cite this Article Govindaswamy, Padavattan, Carroll, Patrick J., Sinha, Chittaranjan and Kollipara, Mohan Rao(2007)'Reactivity studies of (⁶-arene)ruthenium(II) dimers with arylazoimidazole ligands: molecular structure of [(⁶-p-cymene)RuCl(Me-C₆H₄-Nequals;N-C₃H₂N₂-1-CH₃)]PF₆', Journal of Coordination Chemistry, 60:1,97 — 107

To link to this Article: DOI: 10.1080/00958970600731562

URL: <http://dx.doi.org/10.1080/00958970600731562>

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Reactivity studies of (η^6 -arene)ruthenium(II) dimers with arylazoimidazole ligands: molecular structure of $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}(\text{Me-C}_6\text{H}_4\text{-N=N-C}_3\text{H}_2\text{N}_2\text{-1-CH}_3)]\text{PF}_6$

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(Received in final form 17 January 2006)

The complexes $[(\eta^6\text{-arene})\text{Ru}(\mu\text{-Cl})\text{Cl}_2]$ (arene = *p*-cymene (**1**), hexamethylbenzene reacts at low temperature with the arylazoimidazole (RaaiR') ligands 2-(phenylazo)imidazole (Phai-H), 1-methyl-2-(phenylazo)imidazole (Phai-Me), 1-ethyl-2-(phenylazo)imidazole (Phai-Et), 2-(tolylazo)imidazole (Tai-H), 1-methyl-2-(tolylazo)imidazole (Tai-Me) and 1-ethyl-2-(tolylazo)imidazole (Tai-Et) to give complexes of the type $[(\eta^6\text{-arene})\text{RuCl}(\text{RaaiR}')^+]$. The complexes were characterized by FTIR and ¹H NMR and ¹³C {¹H} NMR spectroscopy. The molecular structure of $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}(\text{Me-C}_6\text{H}_4\text{-N=N-C}_3\text{H}_2\text{N}_2\text{-1-CH}_3)]\text{PF}_6$ was established by single-crystal X-ray diffraction methods.

Keywords: *p*-Cymene; Hexamethylbenzene; Arylazoimidazole; Ruthenium; X-ray structure

1. Introduction

The chemistry of half-sandwich (η^6 -arene)ruthenium complexes has been widely developed in the past decade, in part due to their catalytic potential, but also to their usefulness in the synthesis of other Ru(0) and Ru(II) complexes [1–4]. Recently, McNae *et al.* [5] reported the first half-sandwich (arene)ruthenium(II)-enzyme complex which was isolated by the reaction of a (η^6 -*p*-cymene)ruthenium(II) complex with hen egg white lysozyme. (Arene)ruthenium(II) complexes have been the subject of intense research in the field of organometallic chemistry during recent years [6], as has the chemistry of ruthenium with unsaturated nitrogen ligands [7–16]. Photophysical and photochemical properties have been investigated with particular emphasis on *N,N*-chelating pyridine bases and related species [7–16]. Ring size and the substituents in the heterocyclic ring significantly modify π -acidity and regulate the physical and chemical properties of the complexes [17].

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Recently, the design of molecular architectures with imidazole ligands has contributed to the understanding of biomolecular interactions with metal ions and provides models for the active sites of metalloproteins [18–21]. Ruthenium-imidazole complexes are of interest for their antitumor activities [21]. Imidazole bears the azoimine ($-\text{N}=\text{N}-\text{C}=\text{N}-$) functional group, and is an efficient π -acid system for the stabilization of low oxidation states of metal ions. The chemistry of this functional group with platinum is also known in detail [22–24]. We previously reported (cyclopentadienyl)ruthenium(II) and (indenyl)ruthenium(II) complexes containing arylazoimidazole ligands [25], and the reactivity difference between (*p*-cymene)ruthenium(II) and (hexamethylbenzene)ruthenium(II) complexes with pyrazoles, azide and diphenyl-2-pyridyl phosphine [26]. However, no reports are available on these (arene)ruthenium complexes with azoimine ligands. Here we report a study of arylazoimidazole (RaaiR') complexes of (*p*-cymene)ruthenium(II) and (hexamethylbenzene)ruthenium(II). The single-crystal X-ray structure analysis of the representative complex $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}(\text{Me}-\text{C}_6\text{H}_4\text{-N}=\text{N}-\text{C}_3\text{H}_2\text{N}_2\text{-1-CH}_3)]^+$ (**6**) is also presented. The ligands shown below were investigated.

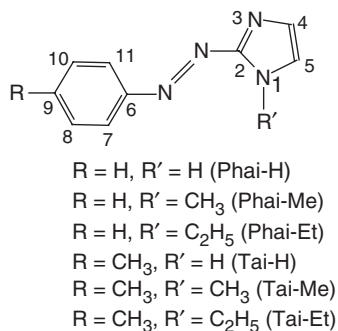


Chart 1

2. Experimental

2.1. Physical measurements

Elemental analysis was performed on a Perkin-Elmer 2400 CHN/O system. IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer (KBr pellets). Electronic spectra were recorded on a Hitachi 300 spectrophotometer (CH_2Cl_2). ^1H NMR and ^{13}C $\{^1\text{H}\}$ NMR spectra (CDCl_3 solvent with TMS as internal standard) were recorded on Jeol 500 (500 MHz) and Bruker ACF-300 (300 MHz) spectrometers; coupling constants J are given in Hz.

2.2. Materials and methods

All chemicals used were of reagent grade. All reactions were carried out in distilled and dried solvents. Ruthenium trichloride trihydrate was purchased from

Arora Matthey Ltd., and used as received. The ligands [22a, 27] and the precursor complexes $[\{\eta^6\text{-arene}\}\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$, arene = *p*-cymene (**1**), hexamethylbenzene (**8**) [28], were prepared by the following literature methods.

2.3. Synthesis of $[\{\eta^6\text{-p-cymene}\}\text{RuCl}(\text{RaaiR}')]\text{PF}_6$ {RaaiR' = *Phai-H* (**2**), *Phai-Me* (**3**), *Phai-Et* (**4**), *Tai-H* (**5**), *Tai-Me* (**6**), *Tai-Et* (**7**)}

A mixture of $[\{\eta^6\text{-p-cymene}\}\text{RuCl}_2]_2$ (**1**) (100 mg, 0.163 mmol) the arylazoimidazole (RaaiR') ligand (0.408 mmol) and NH_4PF_6 (0.408 mmol) was stirred in dry methanol (20 cm³) at -5°C to -10°C (ice/NaCl mixture) for 3 h when the orange product separated out. The compound was filtered off, washed with diethylether and dried under vacuum.

2: yield 150 mg, (78%). IR (cm⁻¹): $\nu_{(\text{N-H})}$ 2925 (s), $\nu_{(\text{C=N})}$ 1633 (s), $\nu_{(\text{N=N})}$ 1394 (s), $\nu_{(\text{P-F})}$ 844 (s). ¹H NMR (δ): 1.13 (d, 3H, $J_{\text{H-H}}=6.72$ Hz, CH₃), 1.24 (d, 3H, $J_{\text{H-H}}=6.72$ Hz, CH₃), 2.16 (s, 3H, CH₃), 2.86 (sep, 1H, CH, cymene), 5.02 (d, 2H, $J_{\text{H-H}}=5.84$ Hz, cymene), 5.32 (d, 2H, $J_{\text{H-H}}=5.84$ Hz, cymene), 6.51 (d, 2H, $J_{\text{H-H}}=7.58$ Hz, Ph), 6.63–6.71 (m, 3H, Ph), 7.73 (d, 1H, $J_{\text{H-H}}=6.38$ Hz, imidazole), 7.92 (d, 1H, $J_{\text{H-H}}=6.42$ Hz, imidazole), 8.23 (s, 1H, NH). ¹³C {¹H} NMR (δ): 17.91, 19.23, 21.47, (CH₃), 29.04 (CH, cymene), 80.95, 81.23, 82.91, 84.14, (CH, cymene), 87.35, 96.46 (C, cymene), 122.35, 124.56, 126.96, 127.37 (Ph), 134.17, 136.26, 147.52 (imidazole). Anal. Calcd for C₁₉H₂₂ClN₄PF₆Ru (%): C, 38.82; H, 3.77; N, 9.53. Found: C, 38.73; H, 3.76; N, 9.16. Electronic spectrum: $\lambda_{\text{max}}=387, 311$ nm.

3: yield 145 mg, (74%). IR (cm⁻¹): $\nu_{(\text{C=N})}$ 1633 (s), $\nu_{(\text{N=N})}$ 1427 (s), $\nu_{(\text{P-F})}$ 844 (s). ¹H NMR (δ): 1.17 (d, 3H, $J_{\text{H-H}}=5.86$ Hz, CH₃), 1.31 (d, 3H, $J_{\text{H-H}}=6.02$ Hz, CH₃), 2.16 (s, 3H, CH₃), 2.82 (sep, 1H, CH, cymene), 3.82 (s, 3H, CH₃), 5.32 (d, 2H, $J_{\text{H-H}}=5.42$ Hz, cymene), 5.61 (d, 2H, $J_{\text{H-H}}=5.42$ Hz, cymene), 6.08 (d, 2H, $J_{\text{H-H}}=6.78$ Hz, Ph), 6.21–6.34 (m, 3H, Ph), 7.04 (d, 1H, $J_{\text{H-H}}=8.56$ Hz, imidazole), 7.33 (d, 1H, $J_{\text{H-H}}=8.66$ Hz, imidazole). ¹³C {¹H} NMR (δ): 19.36, 22.54, 24.33 (CH₃), 28.68 (CH, cymene), 33.17 (CH₃), 79.69, 81.32, 84.36, 87.05 (CH, cymene), 92.16, 98.52 (C, cymene), 124.31, 125.68, 129.49, 132.35, (Ph), 133.61, 135.34, 142.03 (imidazole). Anal. Calcd for C₂₀H₂₄ClN₄PF₆Ru (%): C, 39.91; H, 4.01; N, 9.31; Found: C, 40.03; H, 4.14; N, 9.27. Electronic spectrum: $\lambda_{\text{max}}=388, 312$ nm.

4: yield 190 mg, (94%). IR (cm⁻¹): $\nu_{(\text{C=N})}$ 1639 (s), $\nu_{(\text{N=N})}$ 1440 (s), $\nu_{(\text{P-F})}$ 844 (s). ¹H NMR (δ): 1.13 (d, 3H, $J_{\text{H-H}}=5.56$ Hz, CH₃), 1.32 (d, 3H, $J_{\text{H-H}}=5.82$ Hz, CH₃), 1.33–1.42 (t, 3H, $J_{\text{H-H}}=6.32$ Hz, CH₃), 2.13 (s, 3H, CH₃), 2.85 (sep, 1H, CH, cymene), 4.14–4.25 (q, 2H, $J_{\text{H-H}}=5.12$ Hz, CH₂), 5.47 (d, 2H, $J_{\text{H-H}}=5.86$ Hz, cymene), 5.62 (d, 2H, $J_{\text{H-H}}=5.88$ Hz, cymene), 6.21 (d, 2H, $J_{\text{H-H}}=7.56$ Hz, Ph), 6.53–6.64 (m, 3H, Ph), 7.71 (d, 1H, $J_{\text{H-H}}=8.04$ Hz, imidazole), 7.85 (d, 1H, $J_{\text{H-H}}=8.12$ Hz, imidazole). ¹³C {¹H} NMR (δ): 17.31, 18.92, 21.43, 24.58 (CH₃), 29.36 (CH, cymene), 46.78 (CH₂), 80.91, 82.43, 83.72, 85.17 (CH, cymene), 94.14, 102.37 (C, cymene), 126.41, 127.52, 129.39, 132.44 (Ph), 133.19, 139.62, 145.44 (imidazole). Anal. Calcd for C₂₁H₂₆ClN₄PF₆Ru (%): C, 40.95; H, 4.25; N, 9.09. Found: C, 40.83; H, 4.62; N, 9.02. Electronic spectrum: $\lambda_{\text{max}}=468, 402, 367$ nm.

5: yield 163 mg, (82%). IR (cm⁻¹): $\nu_{(\text{N-H})}$ 3383 (m), $\nu_{(\text{C=N})}$ 1600 (s), $\nu_{(\text{N=N})}$ 1394 (s), $\nu_{(\text{P-F})}$ 850 (s). ¹H NMR (δ): 0.87 (d, 3H, $J_{\text{H-H}}=6.60$ Hz, CH₃), 1.03 (d, 3H, $J_{\text{H-H}}=5.02$ Hz, CH₃), 1.88 (s, 3H, CH₃), 2.15 (s, 3H, CH₃), 2.52 (sep, 1H, CH, cymene), 5.60 (d, 2H, $J_{\text{H-H}}=6.21$ Hz, cymene), 5.71 (d, 2H, $J_{\text{H-H}}=6.15$ Hz, Ph),

5.75 (d, 2H, $J_{\text{H-H}} = 6.25$ Hz, Ph), 5.99 (d, 2H, $J_{\text{H-H}} = 6.25$ Hz, cymene), 7.40 (d, 1H, $J_{\text{H-H}} = 8.28$ Hz, imidazole), 7.92 (d, 1H, $J_{\text{H-H}} = 7.35$ Hz, imidazole), 8.60 (s, 1H, NH). ^{13}C $\{^1\text{H}\}$ NMR (δ): 21.36, 23.83, 26.58, 27.07 (CH_3), 33.17 (CH, cymene), 87.53, 88.12, 89.36, 90.34, (CH, cymene), 94.53, 104.32 (C, cymene), 122.56, 123.41, 125.62, 126.59 (Ph), 134.18, 141.26, 148.12 (imidazole). Anal. Calcd for $\text{C}_{20}\text{H}_{24}\text{ClN}_4\text{PF}_6\text{Ru}$ (%): C, 39.91; H, 4.01; N, 9.31. Found: C, 40.33; H, 4.01; N, 9.15. Electronic spectrum: $\lambda_{\text{max}} = 402, 323$ nm.

6: yield 172 mg, (85%). IR (cm^{-1}): $\nu_{(\text{C}=\text{N})}$ 1600 (s), $\nu_{(\text{N}=\text{N})}$ 1427 (s), $\nu_{(\text{P-F})}$ 844 (s). ^1H NMR (δ): 1.16 (d, 3H, $J_{\text{H-H}} = 3.72$ Hz, CH_3), 1.22 (d, 3H, $J_{\text{H-H}} = 3.60$ Hz, CH_3), 1.99 (s, 3H, CH_3), 2.54 (s, 3H, CH_3), 2.78 (sep, 1H, CH, cymene), 4.19 (s, 3H, CH_3), 5.62 (d, 2H, $J_{\text{H-H}} = 6.44$ Hz, cymene), 5.87 (d, 2H, $J_{\text{H-H}} = 6.44$ Hz, cymene), 6.02 (d, 2H, $J_{\text{H-H}} = 5.67$ Hz, Ph), 7.41 (d, 2H, $J_{\text{H-H}} = 8.46$ Hz, Ph), 7.49 (d, 1H, $J_{\text{H-H}} = 1.26$ Hz, imidazole) 7.97 (d, 1H, $J_{\text{H-H}} = 8.52$ Hz, imidazole). ^{13}C $\{^1\text{H}\}$ NMR (δ): 18.27, 21.30, 21.68, 23.01 (CH_3), 31.15 (CH, cymene), 35.62 (CH_3), 80.78, 85.59, 87.69, 90.53 (CH, cymene), 94.36, 102.57 (C, cymene), 123.91, 126.52, 127.84, 129.88 (Ph), 132.86, 138.42, 144.54 (imidazole). Anal. Calcd for $\text{C}_{21}\text{H}_{26}\text{ClN}_4\text{PF}_6\text{Ru}$ (%): C, 40.95; H, 4.25; N, 9.09. Found: C, 40.69; H, 4.18; N, 9.64. Electronic spectrum: $\lambda_{\text{max}} = 408, 333$ nm.

7: yield 165 mg, (80%). IR (cm^{-1}): $\nu_{(\text{C}=\text{N})}$ 1606 (s), $\nu_{(\text{N}=\text{N})}$ 1434 (s), $\nu_{(\text{P-F})}$ 844 (s). ^1H NMR (δ): 0.88 (d, 3H, $J_{\text{H-H}} = 6.90$ Hz, CH_3), 1.13 (d, 3H, $J_{\text{H-H}} = 6.90$ Hz, CH_3), 1.42–1.45 (t, 3H, $J_{\text{H-H}} = 6.65$ Hz, CH_3), 1.91 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 2.79 (sep, 1H, CH, cymene), 4.52–4.55 (q, 2H, $J_{\text{H-H}} = 6.85$ Hz, CH_2), 5.77 (d, 2H, $J_{\text{H-H}} = 6.10$ Hz, cymene), 6.33 (d, 2H, $J_{\text{H-H}} = 6.14$ Hz, cymene), 7.06 (d, 2H, $J_{\text{H-H}} = 5.39$ Hz, Ph), 7.96 (d, 2H, $J_{\text{H-H}} = 5.36$ Hz, Ph), 8.18 (d, 1H, $J_{\text{H-H}} = 8.58$ Hz, imidazole), 8.31 (d, 1H, $J_{\text{H-H}} = 8.54$ Hz, imidazole). ^{13}C $\{^1\text{H}\}$ NMR (δ): 18.98, 21.71, 22.47, 26.41, 31.22 (CH_3), 39.86 (CH, cymene), 44.23 (CH_2), 79.91, 81.24, 82.46, 85.03 (CH, cymene), 91.93, 97.45 (C, cymene), 123.04, 126.51, 130.47, 131.95 (Ph), 133.87, 135.65, 141.32 (imidazole). Anal. Calcd for $\text{C}_{22}\text{H}_{28}\text{ClN}_4\text{PF}_6\text{Ru}$ (%): C, 41.94; H, 4.48; N, 8.89. Found: C, 41.75; H, 4.52; N, 8.96. Electronic spectrum: $\lambda_{\text{max}} = 398, 304$ nm.

2.4. Synthesis of $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}(\text{RaaiR}')]\text{PF}_6$ {*RaaiR'* = *Phai-H* (9), *Phai-Me* (10), *Phai-Et* (11), *Tai-H* (12), *Tai-Me* (13), *Tai-Et* (14)}

A mixture of $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\mu\text{-Cl})(\text{Cl})_2]$ (**8**) (100 mg, 0.149 mmol), the arylazoimidazole (*RaaiR'*) ligand (0.408 mmol) and NH_4PF_6 (0.408 mmol) was stirred in dry methanol (20 cm^3) at -5°C to -10°C (ice/ NaCl mixture) for 3 h when the brown product separated out from solution. The compound was filtered off, washed with diethylether and dried under vacuum.

9: yield 165 mg, (89%). IR (cm^{-1}): $\nu_{(\text{N-H})}$ 3123 (s), $\nu_{(\text{C}=\text{N})}$ 1633 (s), $\nu_{(\text{N}=\text{N})}$ 1427 (s), $\nu_{(\text{P-F})}$ 50 (s). ^1H NMR (δ): 2.03 (s, 18H, C_6Me_6), 6.83 (d, 2H, 7.12 Hz, Ph), 6.96–7.05 (m, 3H, Ph), 7.37 (d, 1H, $J_{\text{H-H}} = 3.16$ Hz, imidazole), 7.59 (d, 1H, $J_{\text{H-H}} = 5.23$ Hz, imidazole), 8.58 (s, 1H, NH). ^{13}C $\{^1\text{H}\}$ NMR (δ): 23.52 (CH_3 , C_6Me_6), 129.71 (C, C_6Me_6), 131.32, 132.81, 133.73, 135.19 (Ph), 137.59, 142.27, 149.15 (imidazole). Anal. Calcd for $\text{C}_{21}\text{H}_{26}\text{ClN}_4\text{PF}_6\text{Ru}$ (%): C, 40.95; H, 4.25; N, 9.09. Found: C, 40.83; H, 4.36; N, 9.02. Electronic spectrum: $\lambda_{\text{max}} = 474, 367$ nm.

10: yield 158 mg, (84%). IR (cm^{-1}): $\nu_{(\text{C}=\text{N})}$ 1633 (s), $\nu_{(\text{N}=\text{N})}$ 1427 (s), $\nu_{(\text{P-F})}$ 857 (s). ^1H NMR (δ): 2.05 (s, 18H, C_6Me_6), 3.41 (s, 3H, CH_3), 6.23–6.49 (m, 5H, Ph), 7.34 (d, 1H, $J_{\text{H-H}} = 4.18$ Hz, imidazole), 7.62 (d, 1H, $J_{\text{H-H}} = 5.13$ Hz, imidazole).

^{13}C $\{^1\text{H}\}$ NMR (δ): 25.16 (CH_3 , C_6Me_6), 34.27 (CH_3), 124.32 (C, C_6Me_6), 123.56, 125.24, 129.14, 130.31 (Ph), 132.34, 135.53, 145.73 (imidazole). Anal. Calcd for $\text{C}_{22}\text{H}_{28}\text{ClN}_4\text{PF}_6\text{Ru}$ (%): C, 41.94; H, 4.48; N, 8.89. Found: C, 41.77; H, 4.51; N, 8.86. Electronic spectrum: $\lambda_{\text{max}} = 477, 383, 310$ nm.

11: yield 181 mg, (94%). IR (cm^{-1}): $\nu_{(\text{C}=\text{N})}$ 1639 (s), $\nu_{(\text{N}=\text{N})}$ 1434 (s), $\nu_{(\text{P}-\text{F})}$ 844 (s). ^1H NMR (δ): 1.41 (s, 3H, CH_3), 2.03 (s, 18H, CH_3 , C_6Me_6), 4.43 (q, 2H, $J_{\text{H}-\text{H}} = 4.68$ Hz, CH_2), 6.15 (d, 2H, $J_{\text{H}-\text{H}} = 6.08$ Hz, Ph), 6.52 (m, 3H, Ph), 6.97 (d, 1H, imidazole), 7.26 (d, 1H, $J_{\text{H}-\text{H}} = 5.14$, imidazole). ^{13}C $\{^1\text{H}\}$ NMR (δ): 15.32 (CH_3), 22.16 (CH_3 , C_6Me_6), 52.19 (CH_2), 122.26 (C, C_6Me_6), 126.13, 127.03, 130.38, 131.56 (Ph), 134.16, 139.52, 146.13 (imidazole). Anal. Calcd for $\text{C}_{23}\text{H}_{30}\text{ClN}_4\text{PF}_6\text{Ru}$ (%): C, 42.89; H, 4.69; N, 8.70. Found: C, 42.93; H, 4.71; N, 8.74. Electronic spectrum: $\lambda_{\text{max}} = 485, 377, 348$ nm.

12: yield 165 mg, (88%). IR (KBr pellets, cm^{-1}): $\nu_{(\text{N}-\text{H})}$ 3429 (s), $\nu_{(\text{C}=\text{N})}$ 1636 (s), $\nu_{(\text{N}=\text{N})}$ 1440 (s), $\nu_{(\text{P}-\text{F})}$ 850 (s). ^1H NMR (δ): 2.06 (s, 18H, C_6Me_6), 2.54 (s, 3H, CH_3), 7.48 (d, 2H, $J_{\text{H}-\text{H}} = 8.18$ Hz, Ph), 7.69 (d, 2H, $J_{\text{H}-\text{H}} = 8.23$ Hz, Ph), 7.71 (s, 1H, NH), 7.78 (d, 1H, $J_{\text{H}-\text{H}} = 8.36$ Hz, imidazole), 7.92 (d, 1H, $J_{\text{H}-\text{H}} = 9.45$ Hz, imidazole). ^{13}C $\{^1\text{H}\}$ NMR (δ): 20.46 (CH_3 , C_6Me_6), 26.25 (CH_3), 104.84 (C, C_6Me_6), 124.56, 126.48, 127.86, 130.32 (Ph), 134.97, 148.27, 158.19 (imidazole). Anal. Calcd for $\text{C}_{22}\text{H}_{28}\text{ClN}_4\text{PF}_6\text{Ru}$ (%): C, 41.94; H, 4.48; N, 8.89. Found: C, 41.68; H, 4.52; N, 8.81. Electronic spectrum: $\lambda_{\text{max}} = 474, 396, 348$ nm.

13: yield 174 mg, (90%). IR (KBr pellets, cm^{-1}): $\nu_{(\text{C}=\text{N})}$ 1639 (s), $\nu_{(\text{N}=\text{N})}$ 1440 (s), $\nu_{(\text{P}-\text{F})}$ 850 (s). ^1H NMR (δ): 2.04 (s, 18H, C_6Me_6), 2.21 (s, 3H, CH_3), 3.89 (s, 3H, CH_3), 5.46 (d, 2H, $J_{\text{H}-\text{H}} = 4.38$ Hz, Ph), 5.89 (d, 2H, $J_{\text{H}-\text{H}} = 4.46$ Hz, Ph), 7.31 (d, 1H, $J_{\text{H}-\text{H}} = 6.54$ Hz, imidazole), 7.53 (d, 1H, $J_{\text{H}-\text{H}} = 7.28$ Hz, imidazole). ^{13}C $\{^1\text{H}\}$ NMR (δ): 18.39 (CH_3 , C_6Me_6), 23.43 (CH_3), 33.46 (CH_3), 126.52 (C, C_6Me_6), 127.32, 129.48, 131.82, 132.56 (Ph), 134.37, 139.59, 147.62 (imidazole). Anal. Calcd for $\text{C}_{23}\text{H}_{30}\text{ClN}_4\text{PF}_6\text{Ru}$ (%): C, 42.89; H, 4.69; N, 8.70. Found: C, 42.78; H, 4.73; N, 8.74. Electronic spectrum: $\lambda_{\text{max}} = 479, 390, 345$ nm.

14: yield 182 mg, (92%). IR (KBr pellets, cm^{-1}): $\nu_{(\text{C}=\text{N})}$ 1606 (s), $\nu_{(\text{N}=\text{N})}$ 1427 (s), $\nu_{(\text{P}-\text{F})}$ 844 (s). ^1H NMR (δ): 1.32 (t, 3H, $J_{\text{H}-\text{H}} = 7.02$ Hz, CH_3), 2.06 (s, 18H, CH_3 , C_6Me_6), 2.15 (s, 3H, CH_3), 4.26 (m, 2H, $J_{\text{H}-\text{H}} = 5.16$ Hz, CH_2), 6.23 (d, 2H, $J_{\text{H}-\text{H}} = 5.86$ Hz, Ph), 6.35 (d, 2H, $J_{\text{H}-\text{H}} = 6.36$ Hz, Ph), 7.58 (d, 1H, $J_{\text{H}-\text{H}} = 3.32$ Hz, imidazole), 7.92 (d, 1H, $J_{\text{H}-\text{H}} = 6.42$ Hz, imidazole). ^{13}C $\{^1\text{H}\}$ NMR (δ): 18.31 (CH_3), 21.72 (CH_3 , C_6Me_6), 24.24 (CH_3), 48.05 (CH_2), 123.93 (C, C_6Me_6), 118.49, 121.37, 124.12, 126.35 (Ph), 131.51, 134.38, 142.17 (imidazole). Anal. Calcd for $\text{C}_{24}\text{H}_{32}\text{ClN}_4\text{PF}_6\text{Ru}$ (%): C, 43.80; H, 4.90; N, 8.51. Found: C, 43.68; H, 4.96; N, 8.67. Electronic spectrum: $\lambda_{\text{max}} = 469, 332$ nm.

2.5. Structure analysis and refinement

Single crystals of **6** suitable for X-ray analyses were grown by slow diffusion of hexane into a dichloromethane solution of the complex. X-ray intensity data were collected on a Rigaku Mercury CCD area detector employing graphite-monochromated Mo-K α radiation ($\lambda = 0.71069$ Å) at 143 K. Indexing was performed from a series of twelve 0.5° rotation images with exposures of 30 s. Rotation images were processed using CRYSTAL CLEAR [29]. Intensity data were corrected for Lorentz and polarization effects and for absorption using the REQAB program [30]. The structure was solved by direct methods using SIR97 [31] and refined by full-matrix least-squares methods based

Table 1. Crystal data and structure refinement parameters for **6**.

Formula	C ₂₁ H ₂₆ N ₄ PF ₆ ClRu
Formula weight	615.95
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>Z</i>	4
Cell constants (Å, °)	
<i>a</i>	9.6735(7)
<i>b</i>	24.465(2)
<i>c</i>	10.5902(9)
β	102.7160(10)
<i>V</i> (Å ³)	2444.8(3)
Absorption coefficient (cm ⁻¹)	8.79
crystal size (mm ³)	0.38 × 0.27 × 0.10
<i>D</i> _{Calcd} (g cm ⁻³)	1.673
<i>F</i> (000)	1240
2θ range (°)	5.16–54.96
No. reflections measured	11215
No. unique reflections	5374 (<i>R</i> _{int} = 0.0163)
No. observed reflections	5008 (<i>I</i> > 4σ(<i>I</i>))
No. parameters	313
<i>R</i> indices (<i>I</i> > 4σ(<i>I</i>))	<i>R</i> ₁ = 0.0288 <i>wR</i> ₂ = 0.0722
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0312 <i>wR</i> ₂ = 0.0741
GOF	1.051
Final difference peaks (e Å ⁻³)	+0.755, -0.720

on F^2 using SHELXL-97 [32]. Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were refined using a riding model. Refinement converged at final values of $R = 0.0288$ (for observed data F) and $wR_2 = 0.0722$ (for unique data F^2). Table 1 lists cell information, data collection parameters and refinement data. Figure 1 is an ORTEP [33] representation of complex **6** with 30% probability thermal ellipsoids.

3. Results and discussion

1-Methyl-2-(arylo)imidazole (aai-Me), 1-ethyl-2-(arylo)imidazole (aai-Et) and 2-(arylo)imidazole (aai-H) were synthesized by coupling the aryldia-zonium ions with imidazole in aqueous sodium carbonate solution (pH = 7) and purified by the reported method [27]. The alkylation was carried out by adding alkyl halide in dry THF solution to the corresponding 2-(arylo) imidazole in the presence of sodium hydride [34]. The (arene)ruthenium dimers [$\{(\eta^6\text{-arene})\text{Ru}(\mu\text{-Cl})\text{Cl}\}_2$] where arene = *p*-cymene (**1**) and hexamethylbenzene (**8**) reacted with aryloimidazoles (RaaiR') in the presence of ammonium salts in methanol to form mononuclear cationic (arene)ruthenium complexes having the general formula $[(\eta^6\text{-arene})\text{RuCl}(\text{RaaiR}')]^+$ (scheme 1). The complexes are non-hygroscopic, air-stable, shiny crystalline solids. They are sparingly soluble in methanol and benzene, soluble in dichloromethane, chloroform, acetone and acetonitrile, and insoluble in hexane, petroleum ether and diethylether.

IR spectra of the *p*-cymene complexes show strong bands at 1600 and 1394–1440 cm⁻¹ due to $\nu_{\text{C=N}}$ and $\nu_{\text{N=N}}$ of the aryloimidazole (RaaiR'), and a

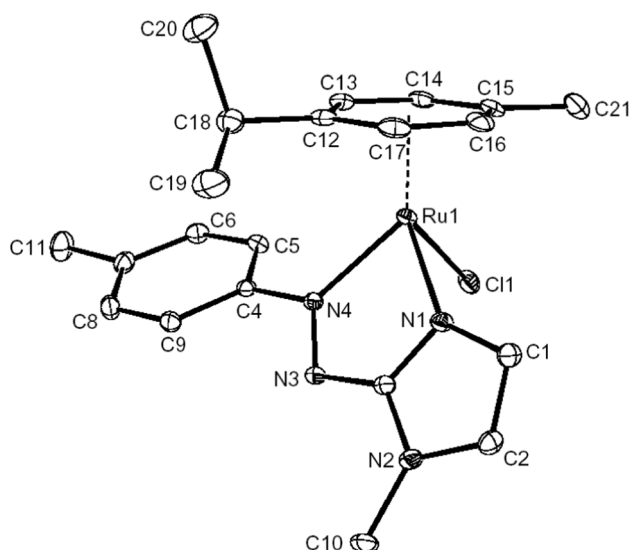
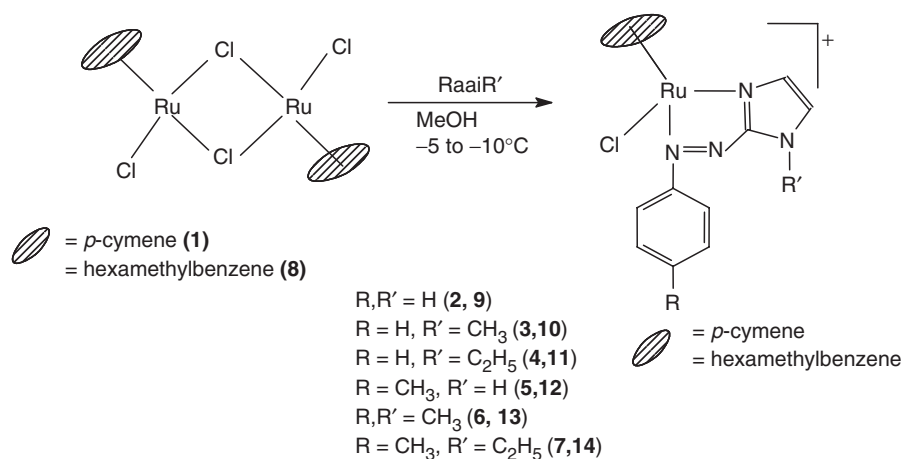


Figure 1. X-ray structure of **6** showing the atom numbering scheme. Hydrogen atoms and PF_6^- are omitted for clarity.



Scheme 1. Preparation of complexes.

strong band at 844 cm^{-1} due to $\nu_{\text{P-F}}$. ^1H NMR spectra of **2–7** exhibit doublets for the methyl protons of the isopropyl group due to the diastereotopic nature of isopropyl group. A septet at 2.52–2.86 ppm is observed for the methine proton of the isopropyl group. The two doublets observed at 5–6 ppm correspond to aromatic *p*-cymene CH protons, shifted downfield as compared to the starting complex **1** due to the cationic nature of the complex. N–H protons of complexes **2** and **5** give peaks in the range 8.2–8.6 ppm. N-methyl protons of **3** and **6** appear as singlets at 3.82 and 4.19 ppm, respectively. The N-methylene protons of **4** and **7** appear as a quartet in the range 4.14–4.55 ppm. All complexes show doublets in the range 5.75–7.96 ppm due to the phenyl protons of the azoimine ligand. In the ^{13}C $\{^1\text{H}\}$ NMR spectra, methyl carbons

give signals in the range 17.31–31.22 ppm. Methyl carbons of the isopropyl group appear at 28.68–39.86 ppm and the cymene carbons at 87.35–104.32 ppm. The signals for carbons of the arene group are similar to those in other reported compounds. Carbons of the imidazole and phenyl groups give signals at 122.35–148.12 ppm.

IR infrared spectra of hexamethylbenzene complexes **9–14** exhibit $\nu_{(N=N)}$ in the range 1427 to 1440 cm^{-1} . In addition, IR spectra contain strong bands at 844–857 cm^{-1} due to $\nu_{(P-F)}$. The formation of complexes **9–14** was conveniently monitored by peak ratios in the ^1H NMR spectra. ^1H NMR spectra exhibit a strong peak at 2.03–2.06 ppm for hexamethylbenzene, which is slightly shifted downfield in comparison to the starting compound **8** (2.02 ppm). The shift may result from a change in electron density at the metal centre due to chelation of the arylazoimidazole. Phenyl protons appear at 6–8 ppm, while the methine protons of imidazole were observed in the range 6.97–7.92 ppm. ^{13}C NMR data are consistent with ^1H NMR data. The methyl carbon of hexamethylbenzene appears around 20 ppm and the ring carbon at ~ 125 ppm. The resonance observed at 118–158 ppm is assigned to the phenyl group and imidazole group of arylazoimidazole (RaaiR') ligand carbons.

The low spin d^6 configuration of the mononuclear complexes provides filled orbitals of proper symmetry, which can interact with the low lying π^* orbitals of the arylazoimidazole ligands (RaaiR'). One should therefore expect a band attributable to the MLCT ($t_{2g} \rightarrow \pi^*$) transition in the electronic spectra [10, 13, 22], where the transition energy of these bands varies with the nature of the ligands acting as π -acceptors. The presence of an electron donating group (H, CH_3 , and C_2H_5) in the imidazole nitrogen of the azoimine ligand should increase the energy of transition, causing a red shift in MLCT maxima [35], while an electron withdrawing group should decrease the transition energy. The electronic spectra of $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}(\text{RaaiR}')]^+$ complexes **2–7** displayed very weak bands at 468 nm; complex **4** showed a medium intensity band at 387–408 nm and a very strong absorption at 304–367 nm. The bands at 468 and 387–408 nm are assigned to MLCT transition [$t_{2g}\{\text{Ru(II)}\} \rightarrow \pi^*(\text{azoimine})$]. The λ_{max} values of this band are consistent with those of the azoimine ligand bound to ruthenium(II) [36].

The free ligand itself shows intra ligand charge-transfer transitions ($n\text{-}\pi^*$, $\pi\text{-}\pi^*$) of high intensity ($\epsilon \sim 10^4\text{--}10^5 \text{ M}^{-1} \text{ cm}^{-1}$) at less than 300 nm. Transitions at ~ 290 nm and below are thus not considered further. Two transitions at longer wavelengths (377–390 nm and 469–485 nm) differ in intensities. The first is of moderate intensity and has been assigned to the MLCT band ($d\pi(\text{Ru}) \rightarrow \pi^*(\text{azoimine})$) in the complexes [22] or else from hybrid orbitals composed of $d\pi(\text{Ru})$ and $\pi(p\text{-cymene}/\text{hexamethylbenzene})$ to the $\pi^*(\text{azoimine})$ orbital of the ligand. The weak transition at 469–485 nm may originate from a singlet–triplet transition, particularly that allowed by strong spin-orbit coupling in ruthenium [37]. Because of better delocalization in the hexamethylbenzene ring the CT bands are shifted to longer wavelengths compared to $p\text{-cymene}$ complexes.

Electronic spectra of hexamethylbenzene complexes **9–14** display bands in the regions 469–485, ~ 380 and ~ 340 nm. The broad medium intensity bands around 380 nm are assigned to MLCT bands arising from drift of electron density from filled $\text{Ru(II)} \rightarrow d\pi(t_{2g})$ orbitals to low lying π^* orbitals of RaaiR'. The position of this band is consistent with those in other metal-azo complexes [38]. The band around 340 nm is assigned to an MLCT transition [$\text{Ru(II)} \rightarrow d\pi^*$ on the hexamethylbenzene ring].

Table 2. Selected bond lengths (Å) and angles (°) for **6**.

Ru(1)–Cl(1)	2.388(5)	Ru(1)–N(1)	2.059(2)	Ru(1)–N(4)	2.073(2)
Ru(1)–C(12)	2.209(2)	Ru(1)–C(13)	2.218(2)	Ru(1)–C(14)	2.206(2)
Ru(1)–C(15)	2.236(2)	Ru(1)–C(16)	2.209(2)	Ru(1)–C(17)	2.181(2)
N(3)–N(4)	1.292(2)	N(4)–C(4)	1.426(2)	N(2)–C(10)	1.470(3)
Ru(1)–C*	1.696(1)				
N(1)–Ru(1)–N(4)	75.4(6)				
N(4)–Ru(1)–Cl(1)	84.45(5)				
N(1)–Ru(1)–Cl(1)	86.49(5)				

*Ruthenium to centroid of *p*-cymene.

4. Molecular structure

Selected bond distances and angles for **6** are given in table 2. The structure shows coordination of the η^6 -*p*-cymene, the bidentate arylazoimidazole ligand and one chloride to form a distorted octahedral geometry. The arylazoimidazole is coordinated through the azo group nitrogen N(4) and imidazole nitrogen N(1) atoms. If we consider the *p*-cymene ring as a single coordination site represented by its centroid, the overall coordination geometry about the metal centre might be regarded as pseudo-tetrahedral or having a typical 'piano-stool' geometry. The *p*-cymene ring is planar and the Ru–C distances are almost equal, with an average bond length of 2.210(2) Å (range 2.181(2)–2.236(2) Å); the ruthenium to *p*-cymene ring centroid distance is 1.6964(1) Å and is consistent with those reported for the other ruthenium(II) η^6 -arene complexes [39]. C–C bond lengths in the *p*-cymene ring are equal and there are no alternate short and long bond lengths; this suggests that there is no localization. The Ru(1)–Cl(1) distance is normal and slightly shorter than the average bond length of 2.3877(5) Å reported for other ruthenium(II) complexes [40]. The bond angles N(4)–Ru(1)–Cl(1), N(1)–Ru(1)–N(4) and N(1)–Ru(1)–Cl(1) are 84.45(5), 75.4(6) and 86.49(5)°, respectively, consistent with the piano stool structure. The N=N bond distance N(3)–N(4) is 1.292(2) Å, longer than the value for the free ligand (1.250(1) Å) [41]. This is due to significant charge delocalization from the metal d-orbitals, namely, the $d\pi(\text{Ru}) \rightarrow \pi^*(\text{azo})$ transition.

Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC 271180. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Acknowledgements

P.G. and K.M.R. express their thanks to V.G. Vaidyanathan, Chemical Laboratory, Central Leather Research Institute (CLRI), Chennai, for providing access to the NMR facility.

References

- [1] M.A. Bennett, M.I. Bruce, T.W. Matheson. In *Comprehensive Organometallic Chemistry*, G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds), Vol. 4, p. 796, Pergamon, Oxford (1982).
- [2] H. Le Bozec, D. Touchard, P.H. Dixneuf. *Adv. Organomet. Chem.*, **29**, 163 (1989).
- [3] M.A. Bennett. In *Comprehensive Organometallic Chemistry II*, E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds), Vol. 7, p. 549, Pergamon, Oxford (1995).
- [4] (a) J. Reedijk. *Chem. Commun.*, 801 (1996); (b) E. Wong, C.M. Giandomenico. *Chem. Rev.*, **99**, 2451 (1999) and references therein.
- [5] I.W. McNae, K. Fishburne, A. Habtemariam, T.M. Hunter, M. Melchart, F. Wong, M.D. Walkinshaw, P.J. Sadler. *Chem. Commun.*, 1786 (2004).
- [6] H.L. Bozec, D. Touchard, P.H. Dixneuf. *Adv. Organomet. Chem.*, **29**, 163 (1989).
- [7] (a) W.T. Wong. *Coord. Chem. Rev.*, **131**, 45 (1994); (b) E.A. Seddon, K.R. Seddon. *The Chemistry of Ruthenium*, Elsevier, Amsterdam (1984).
- [8] (a) D.S. Eggleston, K.A. Goldsby, D.J. Hodgson. *Inorg. Chem.*, **24**, 4573 (1985); (b) B. De Klerk-Engles, H.W. Frawhauf, K. Vrieze, H. Koojiman, A. Spek. *Inorg. Chem.*, **32**, 5528 (1993); (c) C.A. Basel, J.A. Margarucci, J.H. Acquaye, R.S. Rubino, J. Crandall, A.J. Jriricitano, K.J. Takuchi. *Inorg. Chem.*, **32**, 5779 (1993); (d), A. Rudi, Y. Kashaman, D. Gut, F. Lellouche, M. Kol. *Chem. Commun.*, 17, (1997); (e) P.D. Beer, S.W. Dent, G.S. Hobbs, J.J. Wear. *Chem. Commun.*, 99, (1997).
- [9] (a) K. Kalyansundaram, M.S. Lakeeruddin, M.K. Nazeeruddin. *Coord. Chem. Rev.*, **132**, 259 (1994); (b) K. Kalyansundaram. *Coord. Chem. Rev.*, **46**, 159 (1982).
- [10] B.K. Ghosh, A. Chakravorty. *Coord. Chem. Rev.*, **95**, 239 (1989).
- [11] (a) B.K. Santra, G.A. Thakur, P. Ghosh, K.A. Pramanik, G.K. Lahiri. *Inorg. Chem.*, **35**, 3050 (1996); (b) J. Chakravorty, S. Bhattacharya. *Trans. Met. Chem.*, **20**, 138 (1995); (c) T.K. Mallik, P.K. Das, B.K. Roy, B.K. Ghosh. *J. Chem. Res.*, 374 (1993); (d) M. Kakoti, S. Chaudhury, A.K. Deb, S. Goswami. *Polyhedron*, **12**, 783 (1993).
- [12] R.A. Krause, K. Krause. *Inorg. Chem.*, **23**, 2195 (1984); (b) R.A. Krause, K. Krause. *Inorg. Chem.*, **21**, 1714 (1982); (c) R.A. Krause, K. Krause. *Inorg. Chem.*, **19**, 2600 (1980).
- [13] (a) N. Bag, G.K. Lahiri, A. Chakravorty. *Inorg. Chem.*, **31**, 40 (1992); (b) G.K. Lahiri, S. Bhattacharya, S. Goswami, A. Chakravorty. *J. Chem. Soc., Dalton Trans.*, 561 (1990); (c) G.K. Lahiri, S. Goswami, L.R. Falvello, A. Chakravorty. *Inorg. Chem.*, **26**, 3365 (1987).
- [14] (a) B.K. Ghosh, S. Goswami, A. Chakravorty. *Inorg. Chem.*, **22**, 3358 (1983); (b) B.K. Ghosh, A. Mukhopadhyay, S. Goswami, R. Ray, A. Chakravorty. *Inorg. Chem.*, **23**, 4633 (1984).
- [15] (a) R. Argazzi, C.A. Bignozzi, T.A. Heimer, G.J. Meyer. *Inorg. Chem.*, **36**, 2 (1997); (b) C.Y. Hung, T.L. Wang, Y. Jang, W.Y. Kim, K.L. Schmekl, R.P. Thumel. *Inorg. Chem.*, **35**, 5953 (1996); (c) X.M. Chen, W.H. Zang, J. Chen, Y.S. Yang, M.L. Gang. *J. Chem. Soc., Dalton Trans.*, 1767 (1996); (d) A. Real, M.C. Munoz, F. Andress, T. Granier, B. Gallos. *Inorg. Chem.*, **33**, 3587 (1994).
- [16] (a) P. Lincoln, B. Norden. *Chem. Commun.*, 2145 (1996); (b) B.J. Goodfellow, V. Felix, S.M.D. Pacheco, J. Pedrosa de Jesus, M.G.B. Drew. *Polyhedron*, **16**, 393 (1997); (c) C.M. Dupureur, J.K. Barton. *Inorg. Chem.*, **36**, 33 (1997).
- [17] (a) E.C. Constable. *Coord. Chem. Rev.*, **93**, 205 (1989); (b) T. Yamamoto, Z. Zhou, T. Kanbara, M. Shimura, K. Kizu, T. Maruyama, T. Takamura, T. Fukuida, B. Lee, N. Ooba, S. Tomaru, T. Kurihara, T. Kaino, K. Kubota, S. Sasaki. *J. Am. Chem. Soc.*, **118**, 10389 (1996).
- [18] (a) T.C. Higgins, M. Helliwell, C.D. Carner. *J. Chem. Soc., Dalton Trans.*, 2101 (1996); (b) R.C. Halz, F.T. Gobena. *Polyhedron*, **15**, 2779 (1996); (c) J. Abe, Y. Shirai. *J. Am. Chem. Soc.*, **118**, 4705 (1996); (d) C. Tejel, B.F. Villarroya, M.A. Ciriano, L.A. Oro, M. Lanfranchi, A. Tiripicchio, M.T. Camellini. *Inorg. Chem.*, **35**, 4360 (1996); (e) M.C. Rodriquer, I.M. Badaraus, M. Cesario, J. Guilhem, B. Keita, L. Nadjjo. *Inorg. Chem.*, **35**, 7804 (1996).
- [19] (a) M. Melnik, L. Macaskova, C.E. Holloway. *Coord. Chem. Rev.*, **126**, 71 (1993); (b) C. Matthews, W. Clegg, M.R.I. Elsegood, T.A. Leese, D. Thorp, P. Thornton, J.C. Lockhart. *J. Chem. Soc., Dalton Trans.*, 1531 (1996); (c) R. Rajan, R. Rajaram, B.U. Nair, T. Ramasami, S.K. Mondal. *J. Chem. Soc., Dalton Trans.*, 2019 (1996).
- [20] S. Belanger, A.L. Beauchamp. *Inorg. Chem.*, **35**, 7836 (1996).
- [21] (a) C. Anderson, L.L. Beauchamp. *Inorg. Chem.*, **34**, 6065 (1995); (b) A. Hatzidimitriou, A. Gourdon, J. Devillers, J.-P. Launay, E. Mena, E. Amouyal. *Inorg. Chem.*, **35**, 2212 (1996); (c) B.K. Keppler, D. Wehe, H. Endres, N. Rupp. *Inorg. Chem.*, **26**, 8440 (1987).
- [22] (a) T.K. Misra, D. Das, C. Sinha, P.K. Ghosh, C.K. Pal. *Inorg. Chem.*, **37**, 1672 (1998); (b) P. Byabartta, S.K. Jasimuddin, B.K. Ghosh, C. Sinha, A.M.Z. Slawin, J.W. Woollins. *New J. Chem.*, **26**, 1415 (2002); (c) J. Dinda, S.K. Jasimuddin, G. Mostafa, C.-H. Hung, C. Sinha. *Polyhedron*, **23**, 793 (2004).
- [23] U.S. Ray, S.K. Jasimuddin, B.K. Ghosh, M. Monfort, J. Ribas, G. Mostafa, T.-H. Lu, C. Sinha. *Eur. J. Inorg. Chem.*, 250 (2004).

- [24] (a) U. Ray, B. Chand, G. Mostafa, J. Cheng, T.-H. Lu, C. Sinha. *Polyhedron*, **22**, 2587 (2003); (b) U. Ray, D. Banerjee, J.-C. Liou, C.-N. Lin, T.-H. Lu, C. Sinha. *Inorg. Chim. Acta*, **358**, 1019 (2005); (c) J.K. Nag, P.K. Santra, C. Sinha, F.-L. Liao, T.-H. Lu. *Polyhedron*, **20**, 2253 (2001).
- [25] P. Govindaswamy, C. Sinha, M.R. Kollipara. *J. Organomet. Chem.*, **690**, 3465 (2005).
- [26] (a) P. Govindaswamy, Y.A. Mozharivskiy, M.R. Kollipara. *J. Organomet. Chem.*, **689**, 3265 (2004); (b) P. Govindaswamy, P.J. Carroll, Y.A. Mozharivskiy, M.R. Kollipara. *J. Organomet. Chem.*, **690**, 885 (2005); (c) P. Govindaswamy, H.P. Yennawar, M.R. Kollipara. *J. Organomet. Chem.*, **689**, 3108 (2004); (d) P. Govindaswamy, Y.A. Mozharivskiy, M.R. Kollipara. *Polyhedron*, **23**, 3115 (2004).
- [27] R.G. Fargher, F.L. Pyman. *J. Chem. Soc.*, 2217 (1919).
- [28] (a) M.A. Bennett, A.K. Smith. *J. Chem. Soc., Dalton Trans.*, 233 (1974); (b) M.A. Bennett, T.N. Huang, T.W. Matheson, A.K. Smith. *Inorg. Synth.*, **21**, 74 (1985); (c) M.A. Bennett, T.W. Matheson, G.B. Robertson, A.K. Smith, P.A. Tucker. *Inorg. Chem.*, **19**, 1014 (1980).
- [29] *Crystal Structure: Crystal Structure Analysis Package*, Rigaku Corp. Rigaku/MSK (2002).
- [30] R.A. Jacobsen, private communication.
- [31] A. Altomare, M. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. Moliterni, G. Polidori, R. Spagna. *J. Appl. Cryst.*, **32**, 115 (1999).
- [32] G.M. Sheldrick. *SHELXL-97: Program for the Refinement of Crystal Structures*, University of Göttingen, Germany (1997).
- [33] C.K. Johnson. *ORTEP-II: A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations*, Oak Ridge National Laboratory Report ORNL-5138 (1976).
- [34] D. Das, M.K. Nayak, C. Sinha. *Trans. Met. Chem.*, **22**, 172 (1997).
- [35] (a) N.G. Del, V. Morena, N.E. Katz, J. Olabe, P.J. Aymonino. *Inorg. Chim. Acta*, **35**, 183 (1979); (b) D.W. Herlocker, R.S. Drago, V.I. Meek. *Inorg. Chem.*, **5**, 2009 (1966); (c) D.K. Lavalley, M.D. Baughman, M.P. Phillips. *J. Am. Chem. Soc.*, **99**, 718 (1977).
- [36] (a) A.P. Szecey, S.S. Millen, A. Haim. *Inorg. Chim. Acta*, **28**, 189 (1978); (b) A. Mishra, K. Mishra, U.C. Agrawala. *Polyhedron*, **9**, 863 (1990).
- [37] E.M. Kobler, T.J. Meyer. *Inorg. Chem.*, **21**, 3967 (1982).
- [38] I. Chakraborty, S. Sengupta, S. Das, S. Banerjee, A. Chakravorty. *J. Chem. Soc., Dalton Trans.*, 134 (2003).
- [39] (a) S.F. Watkins, F.R. Fronczek. *Acta Crystallogr.*, **B38**, 270 (1982); (b) F.B. McCormick, D.D. Cox, W.B. Gleason. *Organometallics*, **12**, 610 (1993); (c) U. Beck, W. Hummel, H.-B. Burgi, A. Ludi. *Organometallics*, **6**, 20 (1993).
- [40] (a) J.-M. Clear, C.M. O'Connell, J.G. Vos, C.J. Cardin, A.J. Edwards. *Chem. Commun.*, 750 (1980); (b) M.I. Bruce, F.S. Wong, B.W. Skelton, A.H. White. *J. Chem. Soc., Dalton Trans.*, 1398 (1981); (c) R.O. Gould, C.L. Jones, R.D. Robertson, T.A. Stephenson. *J. Chem. Soc., Dalton Trans.*, 129 (1981).
- [41] H.-K. Fun, K. Chinnakali, X.-F. Chen, X.-H. Zhu, X.-Z. You. *Acta Crystallogr.*, **25**, 99 (1999).