DOI: 10.1002/ejic.200901004

Synthetic, Spectral, Structural, and Catalytic Aspects of Some Piano-Stool Complexes Containing 2-(2-Diphenylphosphanylethyl)pyridine

Prashant Kumar,[a] Mahendra Yadav,[a] Ashish Kumar Singh,[a] and Daya Shankar Pandey*[a]

Keywords: Ruthenium / Rhodium / Iridium / N,P ligands / Hydrogen transfer

Reactions of the complexes $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$, $[\{(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl\}_2]$ (η^6-arene = C_6H_6, $C_{10}H_{14}$, and C_6Me_6) and $[\{(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl\}_2]$ (M = Rh, Ir) with 2-(2-diphenylphosphanylethyl)pyridine (PPh_2Etpy) were investigated. Neutral κ^1-*P*-bonded complexes $[(\eta^5\text{-}C_5H_5)Ru(\kappa^1\text{-}P\text{-}PPh_2EtPy)(PPh_3)Cl]$ (**1**) and $[(\eta^6\text{-arene})Ru(\kappa^1\text{-}P\text{-}PPh_2EtPy)Cl_2]$ [arene = C_6H_6, (**2**). $C_{10}H_{14}$, (**3**), and C_6Me_6, (**4**)] were isolated from the reactions of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ and $[\{(\eta^6\text{-arene})\text{-}Ru(\mu\text{-}Cl)Cl\}_2]$ with PPh_2EtPy. Treatment of **1**–**4** with NH_4BF_4/NH_4PF_6 in methanol allows the synthesis of cationic κ^2-*P,N*-chelated complexes $[(\eta^5\text{-}C_5H_5)Ru(\kappa^2\text{-}P,N\text{-}PPh_2EtPy)(PPh_3)]^+$ (**5**) and $[(\eta^6\text{-arene})Ru(\kappa^2\text{-}P\text{-}N\text{-}PPh_2EtPy)Cl]^+$ [arene = C_6H_6, (**6**), C_6H_{14}, (**7**), and C_6Me_6 (**8**)]. On the other hand, the dimers $[\{(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl\}_2]$ (M = Rh or Ir) reacted with PPh_2EtPy in methanol to afford cationic κ^2-*P,N*-chelated complexes $[(\eta^5\text{-}C_5Me_5)M(\kappa^2\text{-}P\text{-}N\text{-}PPh_2EtPy)Cl]^+$ [M = Rh, (**9**); Ir, (**10**)]. Complex **10** reacted with an excess amount of sodium azide or sodium chloride to afford the complexes $[(\eta^5\text{-}C_5Me_5)\text{-}Ir(\kappa^1\text{-}P\text{-}PPh_2EtPy)X_2]$ (X = N_3^- **11**; Cl^-, **12**), establishing the hemilabile nature of the coordinated PPh_2EtPy. The complexes were characterized by elemental analyses and various physicochemical techniques. The molecular structures of **1**, **5**, **6**, **9**, and **10** were determined crystallographically, and the catalytic potentials of **1**–**10** were evaluated towards transfer-hydrogenation reactions under aqueous conditions.

Introduction

Considerable current attention has been paid towards the synthesis and characterization of complexes based on the ligands containing P and N or O donor atoms because of their interesting structural features, reactivity, and catalytic applications.[1] Coordination compounds imparting heterodifunctional ligands possessing both the "soft" phosphorus and "hard" nitrogen or oxygen donors exhibit hemilabile behavior and are extremely useful in transition-metal catalysis.[1–3] P,N donor ligands with π-acceptor phosphorus can stabilize low oxidation states of the metals, and the σ-donor ability of the nitrogen stabilizes higher oxidation states and makes the metals more susceptible towards oxidative-addition reactions. The hard donor ligand easily detaches from the metal center, creating a coordination site required for binding of the substrate during the catalytic cycles. Among the most widely studied P,N donor ligands a prominent position is occupied by pyridyl phosphanes, including chiral derivatives.[4–7] In this regard, 2-(2-diphenylphosphanylethyl)pyridine (PPh_2EtPy) containing both P and N donors have drawn special attention.[8] This phosphane exhibits a versatile coordination behavior and a few transition-metal complexes based on it have been reported.[8c,8d] It may coordinate to metal centers in three different coordination modes: P-monodentate, P,N-bridge, and P,N-chelate mode.[8] In its chelating mode, PPh_2EtPy forms a six-membered chelate ring in the "twist chair conformation" and plays a significant role in the catalytic processes, for example, in carbonylation of alkynes, oligomerization and polymerization of ethene, and in asymmetric transfer hydrogenation.[9–12]

Furthermore, the ruthenium complex $[(\eta^5\text{-}C_5H_5)\text{-}Ru(PPh_3)_2Cl]$ and the dimeric complexes $[\{(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl\}_2]$ (η^6arene = C_6H_6, $C_{10}H_{14}$, and C_6Me_6) and $[\{(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl\}_2]$ (M = Rh or Ir) play a vital role in organometallic chemistry.[13–16] While the reactivity of these precursors with a variety of ligands has been reported, its reactivity with PPh_2EtPy is yet to be explored. It is well established that simple phosphane-containing ruthenium, rhodium, and iridium complexes acts as active catalysts, particularly in presence of a base and incorporation of the $\eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_5Me_5$, and η^6-arene as spectator ligands in the complexes boosts enantioselectivity of the respective reactions.[17,18] With the objective to expand the chemistry of PPh_2EtPy and to develop hydrogen-transfer catalysts containing the $[(\eta^5\text{-}C_5H_5)Ru\text{-}/[(\eta^6\text{-arene})Ru\text{-}/[(\eta^5\text{-}C_5Me_5)Rh\text{-}/[(\eta^5\text{-}C_5Me_5)Ir\text{-}]$ moieties and PPh_2EtPy, we synthesized and characterized a series of new neutral and cationic ruthenium(II) and rhodium(III)/iridium(III) complexes. These rep-

[a] Department of Chemistry, Faculty of Science, Banaras Hindu University,
Varanasi 221005 (U.P.), India
Fax: +91-542 2368174
E-mail: dspbhu@bhu.ac.in

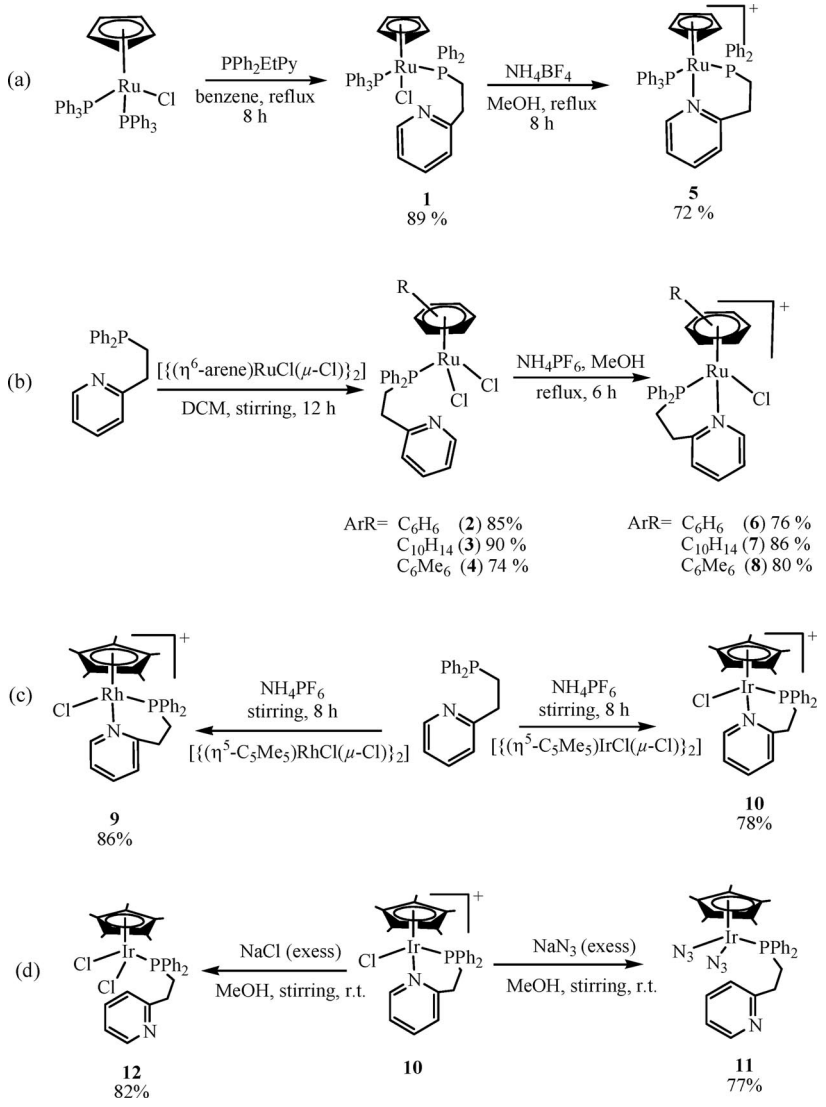
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.200901004.

resent the first examples of complexes containing [(η^5-C_5H_5)Ru-, [(η^6-arene)Ru-, [(η^5-C_5Me_5)Rh-, [(η^5-C_5Me_5)Ir-] moieties and PPh_2EtPy. In this paper we present the synthesis and spectral and structural characterization of some piano-stool ruthenium(II) and rhodium/iridium(III) complexes imparting PPh_2EtPy as a coligand. Also, we describe herein catalytic applications of complexes **1**–**10** in the reduction of ketones to alcohol under aqueous and aerobic conditions.

Results and Discussion

Synthesis of the Complexes

The reaction of the complex [(η^5-C_5H_5)Ru(PPh_3)$_2$Cl] with PPh_2EtPy in benzene under refluxing conditions afforded the P-coordinated neutral complex [(η^5-C_5H_5)Ru(κ^1-*P*-PPh_2EtPy)(PPh_3)Cl] (**1**), whereas its reaction with PPh_2EtPy in methanol yielded the cationic complex [(η^5-C_5H_5)Ru(κ^2-*P*,*N*-PPh_2EtPy)(PPh_3)]$^+$ (**5**) containing κ^2-*P*,*N*-chelated PPh_2EtPy. The synthesis of complex **5** was also achieved by treatment of **1** with NH_4BF_4 in methanol whilst stirring at room temperature (Scheme 1a). The ability of the chlorido-bridged arene ruthenium dimers [{(η^6-arene)Ru(μ-Cl)Cl}$_2$] to form mono- and binuclear complexes of the general formula [(η^6-arene)$RuCl_2L$] and [{(η^6-arene)-$RuCl_2$}$_2$(μ-L)] is well documented.[19] Reactions of the dimers [{(η^6-arene)Ru(μ-Cl)Cl}$_2$] (η^6-arene = C_6H_6, $C_{10}H_{14}$, and C_6Me_6) with PPh_2EtPy in dichloromethane whilst stirring at room temperature afforded the P-coordinated neutral complexes [(η^6-C_6H_6)Ru(κ^1-*P*-PPh_2EtPy)Cl_2] (**2**), [(η^6-$C_{10}H_{14}$)Ru(κ^1-*P*-PPh_2EtPy)Cl_2] (**3**), and [(η^6-C_6Me_6)Ru(κ^1-*P*-PPh_2EtPy)Cl_2] (**4**). Complexes **2**–**4** upon treatment with NH_4PF_6 in methanol under refluxing conditions allows N-coordination of the PPh_2EtPy to ruthenium, affording the P,N-chelated cationic complexes [(η^6-C_6H_6)Ru(κ^2-*P*,*N*-PPh_2EtPy)Cl]PF_6 (**6**), [(η^6-$C_{10}H_{14}$)Ru(κ^2-*P*,*N*-PPh_2EtPy)-Cl]PF_6 (**7**), and [(η^6-C_6Me_6)Ru(κ^2-*P*,*N*-PPh_2EtPy)Cl]PF_6 (**8**) (Scheme 1b). On the other hand, rhodium and iridium dimers [{(η^5-C_5Me_5)M(μ-Cl)Cl}$_2$] (M = Rh or Ir) reacted



Scheme 1.

with PPh_2EtPy in the presence of NH_4PF_6 in methanol to afford the P,N-chelated cationic complexes $[(\eta^5\text{-}C_5Me_5)Rh(\kappa^2\text{-}P\text{-}N\text{-}PPh_2EtPy)Cl]PF_6$ (**9**) and $[(\eta^5\text{-}C_5Me_5)Ir(\kappa^2\text{-}P\text{-}N\text{-}PPh_2EtPy)Cl]PF_6$ (**10**) in reasonably good yields (Scheme 1c).

The hemilabile behavior of the coordinated PPh_2EtPy in κ^2-*P*-*N*-chelated complexes was established from the reactions of the representative complex $[(\eta^5\text{-}C_5Me_5)Ir(\kappa^2\text{-}P\text{-}N\text{-}PPh_2EtPy)Cl]PF_6$ with an excess amount of NaCl and NaN_3 in methanol whilst stirring. As expected, it gave neutral complexes with the formulations $[(\eta^5\text{-}C_5Me_5)Ir(\kappa^1\text{-}P\text{-}PPh_2EtPy)(N_3)_2]$ (**11**) and $[(\eta^5\text{-}C_5Me_5)Ir(\kappa^1\text{-}P\text{-}PPh_2EtPy)Cl_2]$ (**12**), respectively. Taking into account the lability of PPh_2EtPy in complex **10**, which allows coordination of a chloride/azide ligand through the decoordination of the -Ph_2P-N moiety (Scheme 1d), we believe that complexes **5**–**9** will also exhibit analogous behavior.

Characterization

Complexes **1**–**12** are air-stable, nonhygroscopic, crystalline solids soluble in halogenated solvents like chloroform and dichloromethane, but insoluble in benzene, hexane, diethyl ether, and petroleum ether. Characterization of the complexes under study was achieved by standard spectroscopic techniques (IR, FAB-MS, ^1H and $^{31}P\{^1H\}$ NMR, electronic absorption spectral, and electrochemical studies) as well as elemental analyses. All the complexes gave satisfactory elemental analyses. Information about composition of the complexes was also obtained from FAB mass spectral studies. Resulting data along with their assignments are recorded in the Experimental Section; other data and spectra of the complexes are shown in Figure S1–9 (Supporting Information). The position of various peaks and overall fragmentation patterns in the FAB-MS of the respective complexes conformed well to their respective formulations.

X-ray Crystallography

The molecular structures of complexes **1**, **5**, **6**, **9**, and **10** were determined crystallographically. ORTEP views at 30% thermal ellipsoid probability along with the atom numbering scheme are shown in Figures 1, 2, 3, 4, and 5. Details about the data collection, solution, and refinement are summarized in the Experimental Section, and important geometrical parameters (bond lengths and bond angles) are summarized in the captions of Figures 1–5. A common structural feature of these complexes is the typical pianostool geometry about the respective metal center with a change in the η^5-coordinated hydrocarbon ligands and κ^1-*P*-/κ^2-*P,N*-coordinated PPh_2EtPy. In complex **1**, the coordination geometry about the metal center ruthenium is completed by two P donors, one each from the PPh_3 and PPh_2EtPy, the chlorido group, and the cyclopentadienyl ring in a η^5-manner. An analogous arrangement of various groups was observed in complex **5**, except that in this complex the PPh_2EtPy ligand is coordinated to the ruthenium as a chelating P,N-donor ligand, forming a six-membered chelate ring. The $(\eta^6\text{-}C_6H_6)$-ruthenium complex **6** and $(\eta^6\text{-}C_5Me_5)$-rhodium and iridium complexes **9** and **10**, respectively are isostructural with complex **5**. In complexes **5**, **6**, **9**, and **10**, the PPh_2EtPy ligand is coordinated to the respective metal centers as a chelating P,N-donor ligand, forming a six-membered ring with bite angles of 93.98(2), 91.08(19), 84.2(2), and 84.57(10)°, respectively.

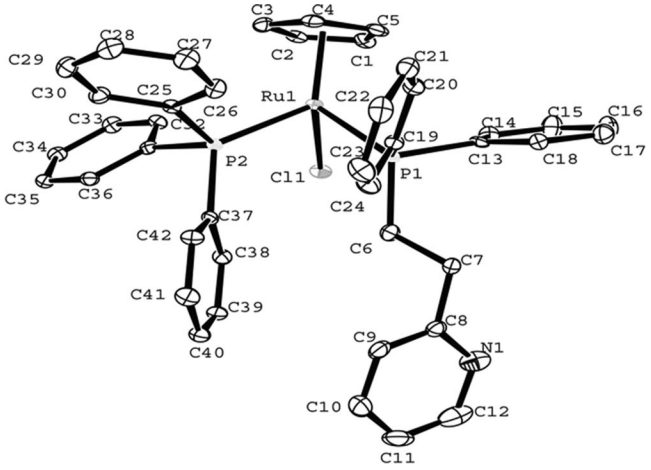


Figure 1. Molecular structure of complex **1** and selected bond length [Å] and angles [°]: Ru1–Cl1 2.448(2), Ru1–P1 2.305(2), Ru1–P2 2.327(2), Ru1–C_{av}(Cp) 2.206(8), Cg-Ru1 1.848, P1–Ru1–P2 97.84(8), P1–Ru1–Cl1 89.10(8), P2–Ru1–Cl1 90.56(8), Cl1–Ru1–Cg 123.9, P1–Ru1–Cg 123.5, P2–Ru1–Cg 122.7.

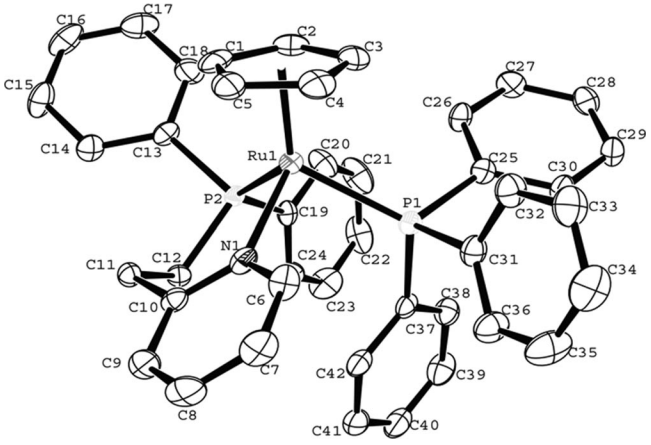


Figure 2. Molecular structure of complex **5** and selected bond length [Å] and angles [°]: Ru1–N1 2.171(3), Ru1–P1 2.3270(8), Ru1–P2 2.3160(8), Ru1–C_{av}(Cp) 2.213(3), Cg-Ru1 1.856, N1–Ru1–P1 90.73(6), N1–Ru1–P2 93.98(7), P2–Ru1–P1 96.07(3), P1–Ru1–Cg 124.9, P2–Ru1–Cg 123.7, N1–Ru1–Cg 119.4.

The hydrocarbon ligands ($\eta^5\text{-}C_5H_5$, **1** and **5**; $\eta^6\text{-}C_6H_6$, **6**; $\eta^6\text{-}C_5Me_5$, **9** and **10**) are planar and various C–C bond lengths in these are normal.[19a,20] Metal-to-centroid distances of the respective hydrocarbon ligands in complexes **1**, **5**, **6**, **9**, and **10** are 1.848, 1.856, 1.711, 1.822, and 1.840 Å, respectively. These are comparable to the values reported in the literature.[20] The Ru–Cl bond lengths in complex **1** and

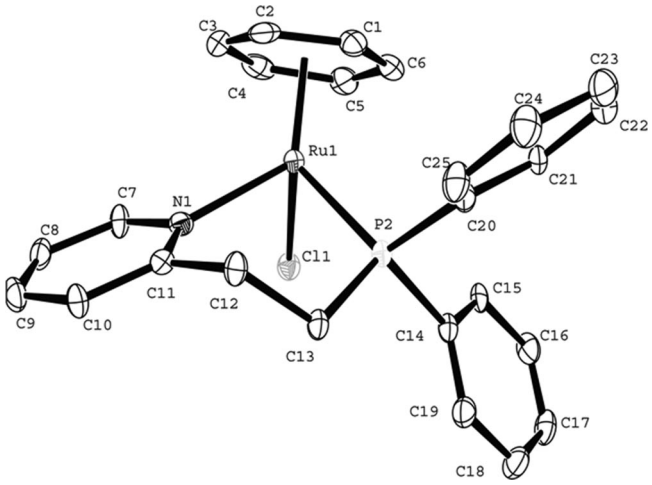


Figure 3. Molecular structure of complex **6** and selected bond length [Å] and angles [°]: Ru1–N1 2.160(7), Ru1–P2 2.333(2), Ru1–C_{av}(arene) 2.219(9), Ru1–Cl1 2.395(2), Cg-Ru1 1.711, N1–Ru1–P2 91.08(19), N1–Ru1–Cl1 83.72(18), P2–Ru1–Cl1 87.86(8), Cl1–Ru1–Cg 126.0, P1–Ru1–Cg 128.6, N1–Ru1–Cg 125.8.

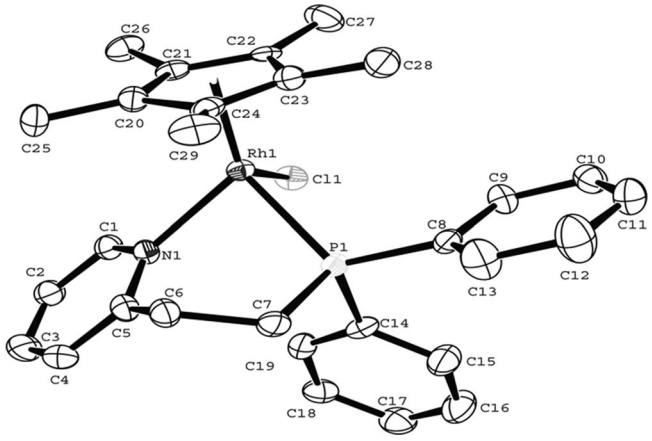


Figure 4. Molecular structure of complex **9** and selected bond length [Å] and angles [°]: Rh1–N1 2.134(7), Rh1–P1 2.318(2), Rh1–C_{av}(arene) 2.189(8), Rh1–Cl1 2.399(2), Cg-Rh1 1.822, N1–Rh1–P1 84.2(2), N1–Rh1–Cl1 91.0(2), P1–Rh1–Cl1 90.77(9), Cl1–Rh1–Cg 120.6, P1–Rh1–Cg 133.1, N1–Rh1–Cg 124.6.

6 are 2.448(2) and 2.395(2) Å, respectively, which are comparable to the Ru–Cl bond lengths in other related complexes.[21,22] Similarly, the Rh–Cl bond length in **9** and the Ir–Cl bond length in **10** are 2.399(2) and 2.402(8) Å, respectively, and are consistent with the values reported in the literature.[21,22] The Ru–P bond lengths in **1**, **5**, and **6** are normal as the Rh–P and Ir–P bonds.[21–23] The Ru–N, Rh–N, and Ir–N bond lengths in the respective complexes are in the range of the reported values.[24]

Crystal structures of **1**, **5**, **6**, **9**, and **10** revealed the presence of extensive intra- and intermolecular C–H···X (X = N, Cl, and F) and C–H···π interactions. These types of interactions play significant roles in the building of huge supramolecular moieties.[25] Interesting motifs resulting from weak bonding interactions (C–H···π interaction) in **1**, **5**, **6**, **9**, and **10** are shown in Figures 6 and 7.

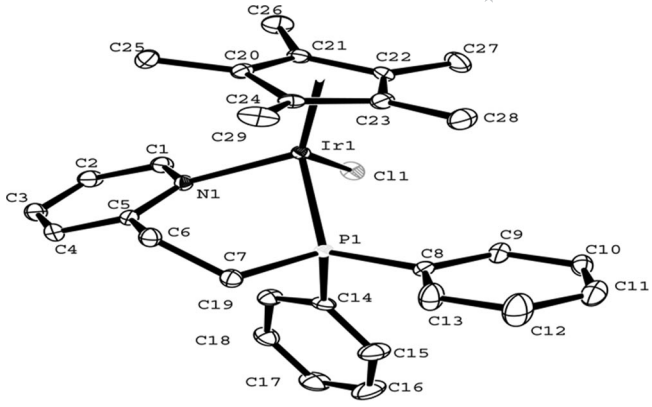


Figure 5. Molecular structure of complex **10** and selected bond length [Å] and angles [°]: Ir1–N1 2.121(3), Ir1–P1 2.308 (11), Ir1–C_{av}(arene) 2.207(4), Ir1–Cl1 2.402 (8), Cg-Ir1 1.840, N1–Ir1–P1 84.57(10), N1–Ir1–Cl1 89.29(9), P1–Ir1–Cl1 90.59(4), Cl1–Ir1–C_g 121.5, P1–Ir1–Cg 133.2, N1–Ir1–Cg 124.6.

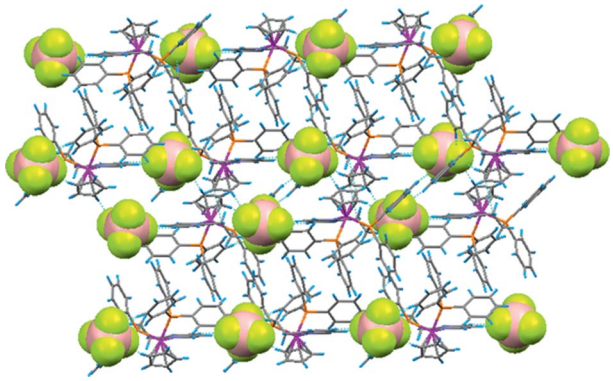


Figure 6. Counteranion (PF_6^-) encapsulated in self-assembled cavity of complex **2**.

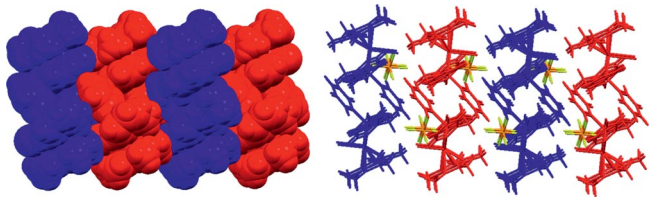


Figure 7. (a) Space-filling representations of **10** showing C–H···F interaction; (b) 1D ladder motif resulting from C–H···F interactions in **10**.

NMR Spectral Studies

The ^1H and $^{31}P\{^1H\}$NMR spectroscopic data of the complexes is gathered in the Experimental Section along with other characterization data. Coordination of PPh_2EtPy to the ruthenium center is evident from the shifts in the position of resonances corresponding to various protons and ^{31}P nuclei in comparison to the precursor complexes. The position and integrated intensity of various signals in the ^1H NMR spectra of the complexes strongly supported the proposed formulations. Formulation of the re-

spective complexes is further supported by ^{31}P NMR spectral studies. Complex **1** in its $^{31}P\{^1H\}$NMR spectrum displayed signals at δ = 44.79 and 37.19 ppm, corresponding to the ^{31}P nuclei of the coordinated PPh_2EtPy and PPh_3, respectively. The signal associated with ^{31}P nuclei of PPh_2EtPy exhibited a significant downfield shift upon coordination to the metal center in comparison to the free ligand (δ =8.43 ppm). Similarly, complex **5** exhibited two signals at δ = 49.68 and 35.90 ppm, assignable to the ^{31}P nuclei of the coordinated PPh_2EtPy and PPh_3, respectively. The $^{31}P\{^1H\}$NMR spectra of complexes **2**–**4** and **6**–**10** displayed singlets at δ = 48.4 (**2**), 47.6 (**3**), 46.9 (**4**), 37.7 (**6**), 36.6 (**7**), 33.5 (**8**), 10.69 (**9**), and 2.40 (**10**) ppm. Observed data suggested that the position of the resonances associated with ^{31}P nuclei of the ligand PPh_2EtPy is sensitive to the metal center and its coordination mode. Upfield shift in the position of signals associated with ^{31}P nuclei may be attributed to the enhanced backdonation from the metal to PPh_2EtPy on going fd **12** exhibited a significant shift [δ = 20.71 (**11**) and 20.79 ppm (**12**)] from that in precursor complex **10** (δ =2.40 ppm) and is in the range of P-coordinated PPh_2EtPy. This observation strongly supported decoordination of PPh_2EtPy from the N-site.

Electronic Spectroscopy

Electronic absorption spectra of complexes **1**–**10** were acquired in dichloromethane (10^{-4} M) solution at room temperature. Resulting data is summarized in the Experimental Section, and the spectra of complexes **1**–**6** are depicted in Figure 8. Ruthenium arene complexes in its absorption spectra usually display intense peaks in the ultraviolet region, corresponding to ligand-based π–π* transitions with overlapping metal-to-ligand (MLCT) transitions in the visible region. An analogous general trend has been observed in the electronic absorption spectra of the complexes under study. Complexes **1**–**4**, containing κ^1-*P* bonded PPh_2EtPy displayed transitions at ca. 612–540, 498–359, and ca. 288–246 nm, whereas the κ^2-*P*-*N* bonded complexes **5**–**10** exhibited transitions at 561–528, 492–351 and ca. 282–241 nm. On the basis of its intensity and position, the lowest-energy absorptions in the visible region have tentatively been assigned to MLCT transition from ruthenium to π* orbitals of $PPh_2EtPy/PPh_3/\eta^n$ bonded hydrocarbon ligands, whereas the bands in the high-energy side have been assigned to the intra-ligand π→π*/ n→π* transitions.[26] One can see that coordination of PPh_2EtPy through both the P and N donor sites in complexes **5**–**10** leads to blueshifting of the $M_{d\pi\rightarrow L^*}$ absorption bands compared to that in **1**–**4**. It may be attributed to the formation of more stable chelated complexes in the twist chair form, which significantly destabilizes the π* orbital of the hydrocarbon ligands (η^5-C_5H_5, **1** and **5**; η^6-C_6H_6, **6**; η^6-C_5Me_5, **9** and **10**).

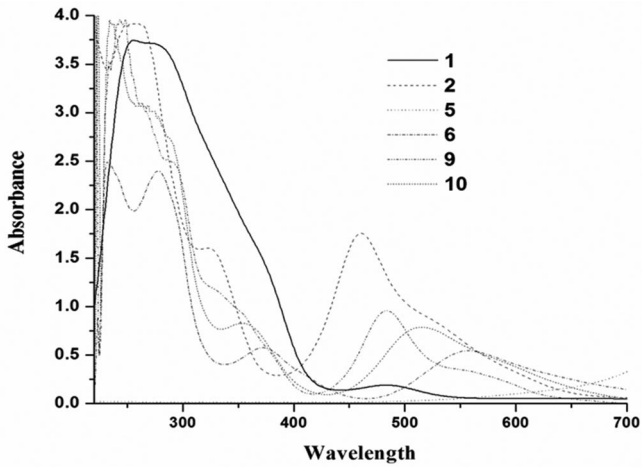


Figure 8. Electronic absorption spectra of complexes **1**, **2**, **5**, **6**, **9**, and **10**.

Electrochemistry

Electrochemical properties of complexes **1**, **2**, **5**, **6**, and **10** were followed by cyclic voltammetry by using 0.1 M tetrabutylammonium perchlorate (TBAP) in dichloromethane as supporting electrolyte. The potential of the Fc/Fc^+ couple under the experimental conditions was 0.10 V (80 mv) vs. Ag/Ag^+. Resulting data is summarized in Table 1, and selected voltammograms are depicted in Figures 9, 10, and 11. Complexes **1** and **5** in their cyclic voltammogram exhibited an oxidative response at 0.82 and 0.26(38) V, respectively, which has been assigned to $Ru^{II/III}$ oxidation. This oxidation is irreversible in **1** and reversible in **5** ($\Delta Ep \approx 100$ mV: $i_{pa} = i_{pc}$). This suggested that the phosphane PPh_2EtPy in complex **5** is bonded to the metal center in a chelating mode. The irreversible reduction peaks at –0.85 (**1**) and –0.83 V (**5**) may be attributed to the ligand-based redox process. Complexes **2** and **6** displayed irreversible and reversible peaks, respectively, at 0.83 and 0.73 V. The redox potential of the $Ru^{II/III}$ couple in complex **6** is higher than that observed in **5**. It may be attributed to the lower electron-donating ability of the η^6-arene ligand in **6** compared to η^5-C_5H_5 in **5**. From the above observations it has been concluded that PPh_2EtPy in a chelating coordination mode is a better stabilizer of the trivalent state of ruthenium compared to the monodentate one. Complex **10** exhibits one electron reversible oxidation corresponding to the $Ir^{IV/III}$ redox couple at ($E_{1/2}{}^{ox}$ vs. Ag/Ag^+) at ca. 1.15(77) V.[27] This suggested that PPh_2EtPy is a better stabilizer of the tetravalent state of iridium in the chelating mode.

Table 1. Cyclic voltammetric data of the complexes.

Complex	$E^0{}_{ox}$ / V (ΔE / mV)	$E^0{}_{ox}$ / V (ΔE / mV)
1	0.82[a]	–0.85
2	0.83[a]	–0.80
5	0.27(83)	–0.83
6	0.73(54)	–0.98
10	1.15(77)	–0.86

[a] Irreversible peak.

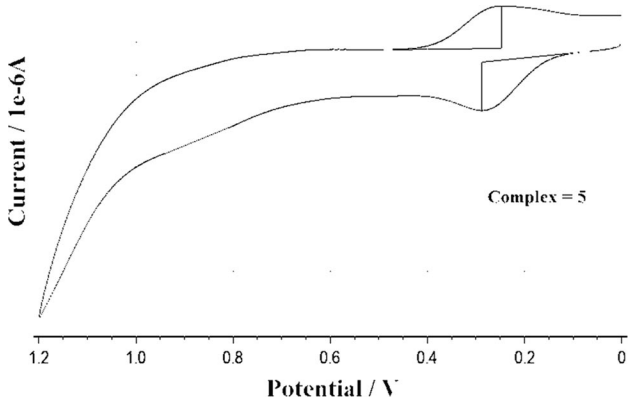


Figure 9. Cyclic voltammogram of **5**.

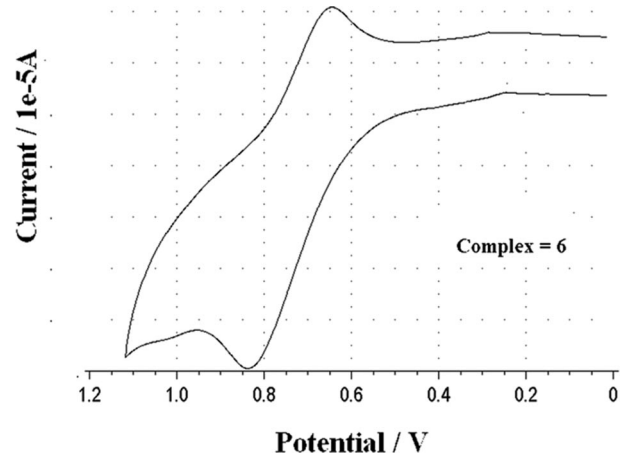


Figure 10. Cyclic voltammogram of **6**.

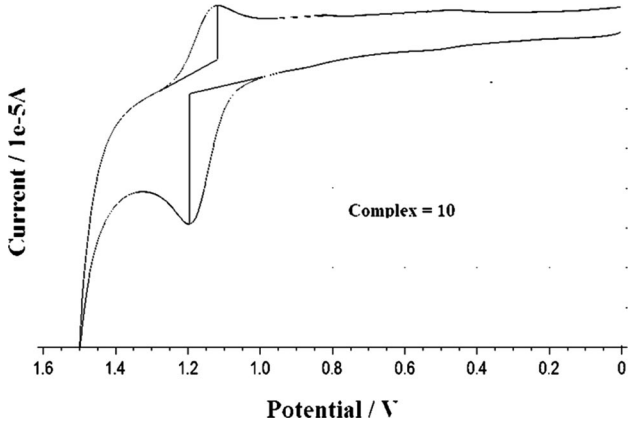
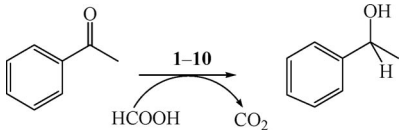


Figure 11. Cyclic voltammogram of **10**.

Catalytic Applications of 1–10 in the Transfer Hydrogenation of Acetophenone under Aqueous Conditions

Hydrogen-transfer reactions of acetophenone using formate as the source of hydrogen were carried out under aqueous and aerobic conditions, and the reaction products were analyzed by ^{1}H NMR spectroscopy. Catalyst testing was conducted to assess the effects of chelating phosphane ligands on the ability of piano-stool complexes to catalyze hydrogen transfer. Of particular interest was the comparison between the ruthenium, rhodium, and iridium complexes and the effect of tethering the phosphane and capping group to make a highly chelating pocket. The reaction chosen for comparison was hydrogen transfer from formate to acetophenone, as this substrate has most commonly been employed in this regard (Scheme 2).



Scheme 2.

Complexes **1**–**10** were tested for the hydrogenation of acetophenone by hydrogen transfer from formate (3.2 mmol; Table 2) by using complexes (6.4 μmol) and the ketone (0.64 mmol) in water (5 mL). The reactions were carried out at 80 °C with a catalyst/substrate/formate (Cat/S/formate) ratio of 1:100:500. The data indicate that complexes **1**–**10** are all reasonably efficient hydrogen-transfer catalysts under aerobic conditions. Conversion versus time plot for PPh_2EtPy containing precursor catalysts **1**, **5**, **7**, **8**, **9**, and **10** is shown in Figure 12. The systems give ca. 50% conversion after 1–4 h, and the relative activity sequence up to ca. 14 h are **10** > **9** > **8** > **4** > **7** > **6** > **2** > **3** > **1** > **5**. The activities of these complexes have been explained on the basis of electron releasing groups present on the aromatic ring and electronic effects about the metal center. It was observed that the presence of electron releasing groups on the aromatic ring increases the electron density on the metal center and the rate of transfer hydrogenation.

Table 2. Transfer hydrogenation of acetophenone catalyzed by ruthenium, rhodium, and iridium complexes.[a]

Catalyst	M(arene)	Conv. / %
1	$[(\eta^5\text{-}C_5H_5)Ru(\kappa^1\text{-}P\text{-}N\text{-}PPh_2EtPy)(PPh_3)Cl]$	75
2	$[(\eta^6\text{-}C_6H_6)Ru(\kappa^1\text{-}P\text{-}PPh_2EtPy)Cl_2]$	84
3	$[(\eta^6\text{-}C_{10}H_{14})Ru(\kappa^1\text{-}P\text{-}PPh_2EtPy)Cl_2]$	82
4	$[(\eta^6\text{-}C_6Me_6)Ru(\kappa^1\text{-}P\text{-}PPh_2EtPy)Cl_2]$	90
5	$[(\eta^5\text{-}C_5H_5)Ru(\kappa^2\text{-}P\text{-}N\text{-}PPh_2EtPy)(PPh_3)]BF_4$	70
6	$[(\eta^6\text{-}C_6H_6)Ru(\kappa^2\text{-}P\text{-}N\text{-}PPh_2EPyt)Cl]PF_6$	86
7	$[(\eta^6\text{-}C_{10}H_{14})Ru(\kappa^2\text{-}P\text{-}N\text{-}PPh_2EtPy)Cl]PF_6$	88
8	$[(\eta^6\text{-}C_6Me_6)Ru(\kappa^2\text{-}P\text{-}N\text{-}PPh_2EtPy)Cl]PF_6$	94
9	$[(\eta^5\text{-}C_5Me_5)Rh(\kappa^2\text{-}P\text{-}N\text{-}PPh_2EtPy)Cl]PF_6$	98
10	$[(\eta^5\text{-}C_5Me_5)Ir(\kappa^2\text{-}P\text{-}N\text{-}PPh_2EtPy)Cl]PF_6$	99

[a] Reaction carried out at 80 °C, in 5 mL water, acetophenone (0.64 mmol), ratio catalyst/substrate/formate being 1:100:500.

In the course of our studies on planar-chiral complexes of late transition metals we prepared planar-chiral arene-phosphane ruthenium/rhodium/iridium complexes (**1**, **5**–**10**) in which anchor phosphane prevents the rotation of the arene ring, constructing a good asymmetric environment around the metal center. Efficiency of the planar-chiral arene-phosphane ligand was proved by the induction of metal-centered chirality with a high selectivity in the ligand exchange reactions with phosphane (PPh_2EtPy) and an-

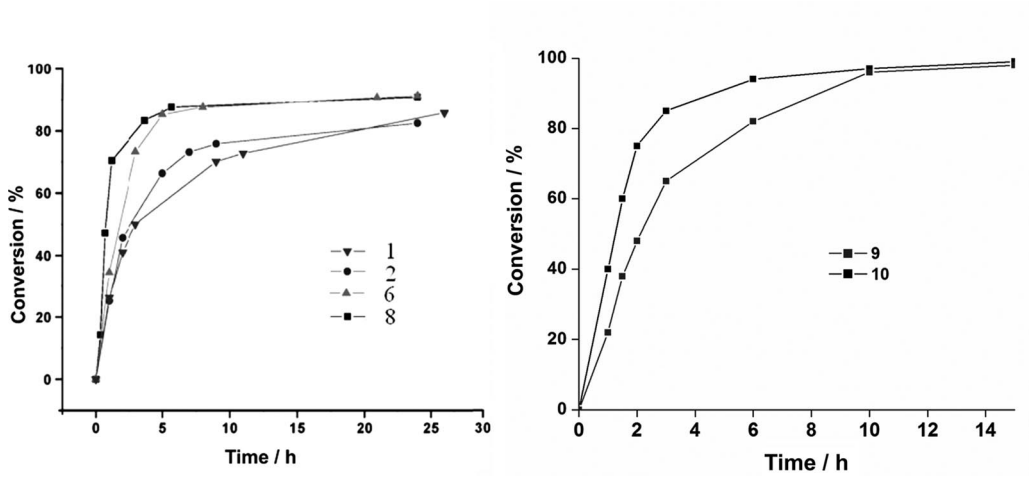


Figure 12. Conversion vs. reaction time plots for complexes **1**, **2**, **6**, **8**, **9**, and **10**.

ionic/neutral ligands. Although, a tentative mechanism of these reactions is described here, a prior step involving formation of the hydrides was thought to be necessary. It is reasonable that these hydrides can be formulated as [Ru(arene)H(L)]$^+$. The partial decoordination of the M–N bond is also necessary to allow coordination of the ketone in complex **5**. On the basis of the behavior of complexes **1**–**10** in solution and the synthesis as shown in Scheme 1, an inner-sphere mechanism[28] is proposed for transfer hydrogenation (TH) of the ketones catalyzed by chelated η^n complexes. Complex **6** interacts with water to form Ru^{II}–OH_2 (**A**), which upon further reaction with formate (source of hydrogen) forms Ru^{II} carboxylate (**B**), which in turn results in the formation of the Ru–H (**D**) intermediate with release of CO_2. Coordination of a ketone with **D** results in the formation of alcohol (Scheme S1, Supporting Information). Formation of Ru–H complexes from Ru–Cl precursors are well documented,[29] and such in situ formed Ru–H species can act as the active catalysts for TH of ketones.[29–32]

Structural and Spectroscopic Correlation between Complexes Containing Chelating *P,N*-PPh_2EtPy

Crystallographic and $^{31}P\{^1H\}$NMR spectroscopic data of some reported complexes and those from the present study involving P,N-chelates are recorded in the Table 3. The literature reports on PPh_2EtPy acting as a P,N-chelate is rather scarce. Six-membered ruthenium chelate rings are in "twist chair" conformation with slightly large bite angles. An increase in the P–M–N angle in the complexes with one chelating rings is observed. It is also clear from Table 3 that shorting of the M–N and M–P bond lengths is in the same direction. This trend shows the effect of relative size and geometry of the coordinating metal on the bite angle and bond lengths. Furthermore, it is observed that the symmetric deformation coordinates S4′[33] depends on the *trans* influence of ligands occupying a position *trans* to P coordination sites and on the M–N bond lengths.

Conclusions

In summary, through this work we have developed a range of piano-stool complexes of Ru, Rh, and Ir by imparting the heterodifunctional phosphane 2-(2-diphenylphosphanylethyl)pyridine. From spectral and structural studies it has been established that the coordinated PPh_2PyEt acts as both the unidentate and the chelating bidentate ligand. In its chelating coordination mode 2-(2-diphenylphosphanylethyl)pyridine forms six-membered chelate rings in the "twist chair" conformation. Furthermore, it has been shown that the complexes under study moderately catalyze reduction of acetophenone to 1-phenylethanol and they serve as hydrogenating catalysts for use in water and air and delivers faster rates in the absence of inert gas protection or substrate solubility in water.

Experimental Section

Reagents: All synthetic manipulations were performed under aerobic conditions. The solvents were rigorously purified by standard

Table 3. Comparison of the structural and ^{31}P NMR spectroscopic data of the metal complexes with one chelating *P,N* PPh_2EtPy.[a]

M	Complex	S4′[b] / °	P-M–N / °	M–N / Å	M–P / Å	δ(P)[c] / ppm	Ref.
Ru	**6**	33.29	91.08	2.159	2.333	37.7	TW
Ru	**5**	37.69	93.98	2.172	2.316	35.9	TW
Pd	Pd(κ^2-*P*-*N*-PPh_2EtPy)(CH_3)Cl	27.78	95.03	2.223	2.196	36.3	[8c]
Ni	Ni(κ^2-*P*-*N*-PPh_2EtPy)Cl_2	22.60	98.03	2.024	2.302	–	[8c]

[a] (PN) chelating *P,N*-PPh_2EtPy, TW = this work. [b] Angular symmetric deformation coordinate S4′ defined as the sum of the M–P–C angles minus the sum of the C–P–C angles. [c] δ (P) is a ^{31}P chemical shift for a chelating phosphane.

procedures prior to their use.[34] Hydrated ruthenium(III) chloride, hydrated rhodium/iridium(III) chloride, dicyclopentadiene pentamethylcyclopentadiene, α-phellandrene, hexamethylbenzene, 2-(2-diphenylphosphanylethyl)pyridine (all Sigma–Aldrich) were used as received without further purifications. The precursor complexes $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$, $[\{(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl\}_2]$ (η^6-arene = C_6H_6, $C_{10}H_{14}$, and C_6Me_6) and $[\{(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl\}_2]$ (M = Rh or Ir) were prepared and purified following literature procedures.[35–37]

General Methods: Elemental analyses for C, H, and N on the complexes were performed with an Exeter Analytical Inc. Model CE-440 elemental analyzer. IR and far-IR in KBr disk form were recorded with a Varian 3300 FTIR spectrophotometer, and electronic absorption spectra were recorded with a Shimadzu UV-1700 spectrophotometer. ^1H (300 MHz), ^{13}C (75.45 MHz), and $^{31}P\{^1H\}$ (121.50 MHz) NMR spectra were acquired with a JEOL AL 300 FTNMR spectrometer at room temperature by using $CDCl_3$ as solvent and TMS as an internal reference for ^1H and H_3PO_4 (85%) as the external reference for $^{31}P\{^1H\}$NMR spectra. FAB mass spectra were recorded with a JEOL SX 102/Da-600 mass spectrometer. Cyclic voltammetric measurements were performed with a CHI 620c electrochemical analyzer. A platinum working electrode, platinum wire auxiliary electrode, and Ag/Ag^+ reference electrode were used in a standard three-electrode configuration. Tetrabutylammonium perchlorate (TBAP) was used as supporting electrolyte, and the solution concentration was ca. 10^{-3}.

$[(\eta^5\text{-}C_5H_5)Ru(\kappa^1\text{-}P\text{-}PPh_2EtPy)(PPh_3)Cl]$ (1): To a suspension of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ (0.5 g, 0.68 mmol) in benzene (25 mL) was added PPh_2EtPy (0.19 g, 0.68 mmol), and the contents of the flask were heated under reflux for 8 h. After cooling to room temperature, the orange solution thus obtained was concentrated to dryness under reduced pressure, and the residue was subjected to purification by silica gel chromatography (CH_2Cl_2/ethyl acetate, 3:1). It gave compound **1** as an orange solid, which was recrystallized from CH_2Cl_2/petroleum ether (40–60 °C). Yield: 0.492 g, 89%. M.p. 145 °C. $C_{42}H_{38}ClNP_2Ru$ (755.24): calcd. C 66.79, H 5.07, N 1.87; found C 66.58, H 5.14, N 1.74. MS (FAB): *m*/*z* (calcd.) = 755.1 (754) $[(\eta^5\text{-}C_5H_5)Ru(\kappa^1\text{-}P\text{-}PPh_2EtPy)(PPh_3)Cl]$, 720.1 (719) $[(\eta^5\text{-}C_5H_5)Ru(\kappa^1\text{-}P\text{-}PPh_2EtPy)(PPh_3)]^+$, 458.2 (456) $[(\eta^5\text{-}C_5H_5)Ru(\kappa^1\text{-}P\text{-}PPh_2EtPy)]^+$. ^1H NMR: δ = 4.64 (s, 5 H, $\eta^5\text{-}C_5H_5$), 9.52 (dd, *J* = 5.2 Hz, 1 H, py-H6), 7.70–7.65 (m, 5 H, py-*H*4 + *Ph*-H2), 7.48–7.38 (m, 6 H, Ph-H3 + -H4), 7.25–7.22 (m, 1 H, py-H5), 7.16 (d, *J* = 7.6 Hz, 1 H, py-H3), 3.21–3.12 (m, 2 H, py-CH_2), 2.33–2.27 (m, 2 H, P-CH_2). ^{13}C NMR: δ = 76.83 (s, Cp), 159.5 (py-C2), 153.8 (py-C6), 138.5 (CH), 133.6 (CH), 131.6 (Ph-C1), 131.2 (CH), 129.0 (CH), 124.6 (s, CH), 123.2 (s, CH), 128.05–138.72 (m, aromatic carbon), 34.3 (py-*C*H_2), 26.1 (*P*-*C*H_2) ppm.$^1P\{^1H\}$NMR: δ = 44.79 (s, *P*Ph_2EtPy), 36.78 (s, *P*Ph_3) ppm. IR (KBr pellet): $\tilde{\nu}$ = 1626 (s), 1440 (s), 1394 (m), 1102 (m), 844 (s), 758 (s), 698 (s) cm^{-1}. UV/Vis: λ (ε, $M^{-1}cm^{-1}$) = 540 (7260), 468 (2680) 371 (6360), 288 (26270) nm.

$[(\eta^6\text{-}C_6H_6)Ru(\kappa^1\text{-}P\text{-}PPh_2EtPy)Cl_2]$ (2): To a stirred solution of $[\{(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)Cl\}_2]$ (0.50 g, 1.0 mmol) in dichloromethane (25 mL) was added PPh_2EtPy (0.34 g, 1.2 mmol), and the resulting solution was stirred for 4 h at room temperature. The red solution thus obtained was filtered to remove any solid impurities, and the filtrate was concentrated to half its volume. The concentrated solution was saturated with petroleum ether (40–60 °C) and left in a refrigerator for crystallization. Slowly, a microcrystalline product separated, which was filtered, washed with diethyl ether, and dried in vacuo. Yield: 0.421 g, 85%. $C_{25}H_{24}Cl_2NPRu$ (541.42): calcd. C 55.46, H 4.47, N 2.59; found C 55.58, H 4.54, N 2.68. MS (FAB): *m*/*z* (calcd.) = 513.3 (512) $[(\eta^6\text{-}C_6H_6)Ru(\kappa^1\text{-}P\text{-}PPh_2EtPy)Cl_2]$, 222 (221) $[(\eta^6\text{-}C_6H_6)RuCl_2]$. ^1H NMR: δ = 9.48 (dd, *J* = 5.2 Hz, 1 H, py-H6), 7.74–7.70 (m, 5 H, py-H4 + Ph-H2), 7.48–7.32 (m, 6 H, Ph-H3 + H4), 7.25–7.22 (m, 1 H, py-H5), 7.20 (d, *J* = 7.6 Hz, 1 H, py-H3), 5.68 (s, 6 H, C_6H_6), 3.20–3.16 (m, 2 H, py-CH_2), 2.40–2.37 (m, 2 H, P-CH_2) ppm. ^{13}C NMR: δ = 88.43 (C-C_6H_6), 154.3 (py-C2), 152.8 (py-C6), 136.4 (CH), 136.6 (CH), 129.6 (Ph-C1), 134.2 (CH), 131.0 (CH), 122.6 (s, CH), 123.2 (s, CH), 35.2 (py-*C*H_2), 25.1 (P-*C*H_2) ppm. $^{31}P\{^1H\}$ NMR: δ = 48.48 (s, *P*Ph_2EtPy) ppm. IR (KBr pellet): $\tilde{\nu}$ = 1648 (s), 1460 (s), 1440 (m), 1378 (m), 1341 (s), 1245 (m), 1195 (m), 1033 (m), 993 (s), 889 (s), 807 (s), 722 (m), 670 (s), 528 (s), 473 (s) cm^{-1}. UV/Vis: λ (ε, $M^{-1}cm^{-1}$) = 568 (1760), 482 (6850), 300 (27070), 246 (39300) nm.

$[(\eta^6\text{-}C_{10}H_{14})Ru(\kappa^1\text{-}P\text{-}PPh_2EtPy)Cl_2]$ (3): Prepared by following the procedure for **2** by using $[\{(\eta^6\text{-}C_{10}H_{14})Ru(\mu\text{-}Cl)Cl\}_2]$ (0.612 g, 1.0 mmol) and PPh_2EtPy (0.291 g, 1.0 mmol). Yield: 0.532 g, 90%. M.p. 140 °C. $C_{29}H_{32}Cl_2NPRu$ (597.53): calcd. C 58.29, H 5.40, N 2.34; found C 58.33, H 5.48, N 2.30. MS (FAB): *m*/*z* (calcd.) = 597.5 (596) $[Ru(\eta^6\text{-}C_{10}H_{14})(\kappa^1\text{-}P\text{-}N\text{-}PPh_2EtPy)Cl_2]$, 306.4 (306) $[(\eta^6\text{-}C_{10}H_{14})RuCl_2]$. ^1H NMR: δ = 9.46 (dd, *J* = 5.0 Hz, 1 H, py-H6), 7.76–7.68 (m, 5 H, py-H4 + Ph-H2), 7.46–7.34 (m, 6 H, Ph-H3 + -H4), 7.25–7.22 (m, 1 H, py-H5), 7.16 (d, *J* = 7.6 Hz, 1 H, py-H3), 5.22 [d, *J* = 5.8 Hz, 2 H, $C_{10}H_{14}(C_6H_4)$], 5.39 [d, *J* = 5.9 Hz, 2 H, $C_{10}H_{14}(C_6H_4)$], 3.18–3.16 (m, 2 H, py-CH_2), 2.98 (sept., 1 H, C*H*), 2.43–2.37 (m, 2 H, P-CH_2), 2.23 (s, 3 H, *C*H_3), 1.30 (d, *J* = 6.96 Hz, 6 H, CH_3) ppm. ^{13}C NMR: δ = 18.60 (C-CH_3), 22.05 $[CH(CH_3)_2]$, 30.60 $[CH(CH_3)_2]$, 84.70 (C-C_6H_4), 100.49 (C-CH_3), 102.16 (C-$CHMe_2$), 159.5 (py-C2), 153.8 (py-C6), 138.5 (CH), 133.6 (CH), 131.6 (Ph-C1), 131.2 (CH), 129.0 (CH), 124.6 (s, CH), 123.2 (s, CH), 34.3 (py-*C*H_2), 26.1 (P-*C*H_2) ppm. $^{31}P\{^1H\}$NMR: δ = 47.65 (s, *P*Ph_2EtPy) ppm. IR (KBr pellet): $\tilde{\nu}$ = 1626 (s), 1445 (s), 1439 (s), 1394 (m), 1102 (m), 848 (s), 758 (s), 698 (s) cm^{-1}. UV/Vis: λ (ε, $M^{-1}cm^{-1}$) = 572 (3260), 495 (8770), 359 (7260), 277 (23080) nm.

$[(\eta^6\text{-}C_6Me_6)Ru(\kappa^1\text{-}P\text{-}PPh_2EtPy)Cl_2]$ (4): Prepared by following the procedure for **2** except that $[\{(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-}Cl)Cl\}_2]$ (0.668 g, 1.0 mmol) was used in place of $[\{(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)Cl\}_2]$. Yield: 0.743 g, 74%. $C_{31}H_{36}Cl_2NPRu$ (625.58): calcd. C 59.52, H 5.80, N 2.24; found C 59.58, H 5.78, N 2.26. MS (FAB): *m*/*z* (calcd.) = 625.5 (624) $[(\eta^6\text{-}C_6Me_6)Ru(\kappa^1\text{-}P\text{-}PPh_2EtPy)Cl_2]$, 334.4 (334), $[(\eta^6\text{-}C_6Me_6)RuCl_2]$. ^1H NMR: δ = 9.48 (dd, *J* = 5.2 Hz, 1 H, py-H6), 7.74–7.70 (m, 5 H, py-H4 + Ph-H2), 7.46–7.32 (m, 6 H, Ph-H3 + -H4), 7.26–7.21 (m, 1 H, py-H5), 7.24 (d, *J* = 7.6 Hz, 1 H, py-H3), 3.26–3.17 (m, 2 H, py-CH_2), 2.41–2.38 (m, 2 H, P-CH_2), 2.08 (s, 18 H, C_6Me_6) ppm. ^{13}C NMR: δ = 15.09 $[\eta^6\text{-}C_6(CH_3)_6]$, 95.94 $[C_6(CH_3)_6]$, 159.5 (py-C2), 153.8 (py-C6), 138.5 (CH), 133.6 (CH), 131.6 (Ph-C1), 131.2 (CH), 129.0 (CH), 124.6 (s, CH), 123.2 (s, CH), 34.3 (py-*C*H_2), 26.1 (P-*C*H_2) ppm. $^{31}P\{^1H\}$NMR: δ = 46.95 (s, *P*Ph_2EtPy) ppm. IR (KBr pellet): $\tilde{\nu}$ = 1668 (s), 1460 (s), 1437 (m), 1378 (m), 1341 (s), 1245 (m), 1195 (m), 1033 (m), 993 (s), 889 (s), 807 (s), 722 (m), 670 (s), 528 (s), 473 (s) cm^{-1}. UV/Vis: λ (ε, $M^{-1}cm^{-1}$) = 612 (1200), 577 (2720), 498 (8210), 331 (11380), 286 (25140) nm.

$[(\eta^5\text{-}C_5H_5)Ru(\kappa^2\text{-}P\text{-}N\text{-}PPh_2EtPy)(PPh_3)]BF_4$ (5)

Method 1: To a suspension of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ (0.5 g, 0.68 mmol) in methanol (25 mL) was added PPh_2EtPy (0.196 g, 0.748 mmol) and NH_4BF_4 (0.078 g, 0.748 mmol), and the mixture was stirred at room temperature for 2 h. It gave a yellow solution, which was filtered to remove any solid impurities. The filtrate was concentrated to half its volume and left for slow crystallization in a refrigerator. Slowly, a microcrystalline product separated, which was filtered, washed with diethyl ether, and dried in vacuo. Yield: 0.432 g, 72%. M.p. 140 °C. $C_{42}H_{38}BF_4NP_2Ru$ (806.59): calcd. C

62.54, H 4.75, N 1.74; found C 62.58, H 4.72, N 1.64. MS (FAB): *m/z* (calcd.) = 719.7 (718) [Ru(η^5-C_5H_5)(κ^2-*P*-*N*-PPh_2EtPy)-(PPh_3)]$^+$, 457.7 (456) [(η^5-C_5H_5)Ru(κ^2-*P*-*N*- PPh_2EtPy)]$^+$. ^{1}H NMR: δ = 9.54 (dd, *J* = 5.5 Hz, 1 H, py-H6), 7.71–7.63 (m, 5 H, py-H4 + Ph-H2), 7.48–7.38 (m, 6 H, Ph-H3 + -H4), 7.25–7.22 (m, 1 H, py-H5), 7.16 (d, *J* = 7.6 Hz, 1 H, py-H3), 4.68 (s, 5 H, η^5-C_5H_5), 3.21–3.12 (m, 2 H, py-CH_2), 2.33–2.27 (m, 2 H, P-CH_2) ppm. ^{13}C NMR: δ = 77.65 (s, Cp), 159.5 (py-C2), 153.8 (py-C6), 138.5 (CH), 133.6 (CH), 131.6 (Ph-C1), 131.2 (CH), 129.0 (CH), 124.6 (s, CH), 123.2 (s, CH), 130.15–136.27 (m, aromatic carbon), 34.3 (py-*C*H_2), 26.1 (P-*C*H_2) ppm. ^{31}P{^{1}H}NMR: δ = 35.90 (s, *P*Ph_2EtPy), 49.68 (s, PPh_3) ppm. IR (KBr pellet): $\tilde{\nu}$ = 1630 (s), 1445 (s), 1394 (m), 1102 (m), 1040 (m), 844 (s), 758 (s), 698 (s) cm^{-1}. UV/Vis: λ (ε, M^{-1}cm^{-1}) = 519 (8090), 415 (1070), 359 (8490), 277 (30090) nm.

Method 2: To a suspension of [(η^5-C_5H_5)Ru(κ^1-*P*-PPh_2EtPy)-(PPh_3)Cl] (**1**; 0.598 g, 1.0 mmol) in methanol (25 mL) was added NH_4PF_6 (0.078 g, 0.748 mmol), and the mixture was stirred at room temperature for 4 h. The clear orange yellow solution was then concentrated. The residue was extracted with dichloromethane and filtered to remove any insoluble material. From the filtrate, **5** was isolated in ca. 78% yield.

[(η^6-C_6H_6)Ru(κ^2-*P*-*N*-PPh_2EtPy)Cl]PF_6·CH_2Cl_2 (6): To a suspension of [(η^6-C_6H_6)Ru(κ^1-*P*-PPh_2EtPy)Cl_2] (0.720 g, 1.0 mmol) in methanol (25 mL) was added NH_4PF_6 (0.062 g, 0.843 mmol), and the mixture was heated to reflux for 4 h. The clear reddish yellow solution was evaporated to dryness under reduced pressure. The residue was extracted with dichloromethane and filtered to remove any insoluble material. The filtrate was saturated with petroleum ether and left for slow crystallization. It gave a fine crystalline product, which was separated by filtration, washed a couple of times with diethyl ether, and dried in vacuo. Yield: 0.611 g, 76%. $C_{26}H_{26}Cl_3F_6NP_2Ru$ (735.87): calcd. C 42.45, H 3.57, N 1.91; found C 42.48, H 3.62, N 1.86. MS (FAB): *m/z* (calcd.) = *m/z* 506.3 (505) [(η^6-C_6H_6)Ru(κ^2-*P*-*N*-PPh_2EtPy)Cl]$^+$, 471.3 (470) [(η^6-C_6H_6)-Ru(κ^2-*P*-*N*-PPh_2EtPy)]$^{2+}$. ^{1}H NMR: δ = 9.78 (dd, *J* = 5.8 Hz, 1 H, py-H6), 7.76–7.66 (m, 5 H, py-H4 + Ph-H2), 7.42–7.36 (m, 6 H, Ph-H3 + -H4), 7.27–7.24 (m, 1 H, py-H5), 7.18 (d, *J* = 7.8 Hz, 1 H, py-H3), 4.64 (s, 5 H, η^5-C_5H_5), 3.24–3.16 (m, 2 H, py-CH_2), 2.36–2.28 (m, 2 H, P-CH_2) ppm. ^{13}C NMR: δ = 88.43 (C-C_6H_6), 154.3 (py-C2), 152.8 (py-C6), 136.4 (CH), 136.6 (CH), 129.6 (Ph-C1), 134.2 (CH), 131.0 (CH), 122.6 (s, CH), 123.2 (s, CH), 35.2 (py-*C*H_2), 25.1 (P-*C*H_2) ppm. ^{31}P{^{1}H} NMR: δ = 37.71 (s, *P*Ph_2PyEt) ppm. UV/Vis: λ (ε, M^{-1}cm^{-1}) = 558 (5470), 377 (5610), 279 (23630) nm.

[(η^6-$C_{10}H_{14}$)Ru(κ^2-*P*-*N*-PPh_2EtPy)Cl]PF_6 (7): Prepared by following the procedure for **6** starting from [(η^6-$C_{10}H_{14}$)Ru(κ^1-*P*-PPh_2EtPy)Cl_2] (0.755 g, 1.0 mmol). Yield: 0.634 g, 86%. M.p. 140 °C. $C_{29}H_{32}ClF_6NP_2Ru$ (707.04): calcd. C 49.26, H 4.56, N 1.98; found C 49.30, H 4.64, N 1.84. MS (FAB): *m/z* (calcd.) = 562.04 (562) [(η^6-$C_{10}H_{14}$)Ru(κ^2-*P*-*N*-PPh_2EtPy)Cl]$^+$, 526.5 (526) [(η^5-$C_{10}H_{14}$)Ru(κ^2-*P*-*N*-PPh_2EtPy)]$^{2+}$, 235.4 (235) [(η^5-$C_{10}H_{14}$)Ru]$^{2+}$. ^{1}H NMR: δ = 9.46 (dd, *J* = 5.0 Hz, 1 H, py-H6), 7.76–7.68 (m, 5 H, py-H4 + Ph-H2), 7.46–7.34 (m, 6 H, Ph-H3 + -H4), 7.25–7.22 (m, 1 H, py-H5), 7.16 (d, *J* = 7.6 Hz, 1 H, py-H3), 5.24 [d, *J* = 5.8 Hz, 2 H, $C_{10}H_{14}(C_6H_4)$], 5.42 [d, *J* = 5.9 Hz, 2 H, $C_{10}H_{14}(C_6H_4)$], 3.18–3.16 (m, 2 H, py-CH_2), 2.96 (sept., 1 H), 2.43–2.37 (m, 2 H, P-CH_2), 2.28 (s, 3 H, CH_3), 1.34 (d, *J* = 6.92 Hz, 6 H, CH_3) ppm. ^{13}C NMR: δ = 18.65 (C-CH_3), 22.12 [CH-(CH_3)$_2$], 32.60 [$CH(CH_3)_2$], 85.70 (C_6H_4), 102.54 (C-CH_3), 104.61 (C-$CHMe_2$), 162.5 (py-C2), 155.8 (py-C6), 140.5 (CH), 136.6 (CH), 134.6 (Ph-C1), 134.2 (CH), 129.0 (CH), 124.6 (s, CH), 123.2 (s, CH), 35.6 (py-*C*H_2), 26.4 (P-*C*H_2) ppm. ^{31}P{^{1}H} NMR: δ = 36.65 (s, *P*Ph_2EtPy) ppm. IR (KBr pellet): $\tilde{\nu}$ = 1664 (s), 1440 (s), 1435 (s), 1394 (m), 1244 (m), 1102 (m), 844 (s), 758 (s), 698 (s), 840 $\nu(PF_6^-)$ cm^{-1}. UV/Vis: λ (ε, M^{-1}cm^{-1}) = 545 (9560), 489 (17290), 352 (15900), 282 (39110) nm.

[(η^6-C_6Me_6)Ru(κ^2-*P*-*N*-PPh_2EtPy)Cl]PF_6 (8): Prepared by following the procedure for **6** by using [(η^6-C_6Me_6)Ru(κ^1-*P*-PPh_2EtPy)-Cl_2] (0.727 g, 1.0 mmol). Yield: 0.628 g, 80%. $C_{31}H_{36}ClF_6NP_2Ru$ (735.09): calcd. C 50.65, H 4.94, N 1.91; found C 50.68, H 4.98, N 1.92. MS (FAB): *m/z* (calcd.) = 590 (589) [(η^6-C_6Me_6)Ru(κ^2-*P*-*N*-PPh_2EtPy)Cl], 554.4 (554) [(η^6-C_6Me_6)Ru(κ^2-*P*-*N*-PPh_2EtPy)], 263.4 (262) [(η^6-C_6Me_6)RuCl]. ^{1}H NMR: δ = 9.48 (dd, *J* = 5.2 Hz, 1 H, py-H6), 7.74–7.70 (m, 5 H, py-H4 + Ph-H2), 7.46–7.32 (m, 6 H, Ph-H3 + -H4), 7.26–7.21 (m, 1 H, py-H5), 7.24 (d, *J* = 7.6 Hz, 1 H, py-H3), 3.22–3.17 (m, 2 H, py-CH_2), 2.41–2.38 (m, 2 H, P-CH_2), 2.08 (s, 18 H, C_6Me_6) ppm. ^{13}C NMR: δ = 15.03 [η^6-$C_6(CH_3)_6$], 88.64 [$C_6(CH_3)_6$], 155.5 (py-C2), 151.8 (py-C6), 136.4 (CH), 132.5 (CH), 132.3 (Ph-C1), 130.2 (CH), 128.4 (CH), 122.4 (s, CH), 120.2 (s, CH), 35.3 (py-*C*H_2), 24.1 (P-*C*H_2) ppm. ^{31}P{^{1}H} NMR: δ = 33.54 (s, *P*Ph_2EtPy) ppm. IR (KBr pellet): $\tilde{\nu}$ = 1648 (s), 1460 (s), 1440 (m), 1378 (m), 1341 (s), 1245 (m), 1195 (m), 1033 (m), 993 (s), 889 (s), 807 (s), 722 (m), 670 (s), 528 (s), 473 (s) cm^{-1}. UV/Vis: λ (ε, M^{-1}cm^{-1}) = 550 (6770), 492 (14350), 351 (16060), 242 (38810) nm.

[(η^5-C_5Me_5)Rh(κ^2-*P*–*N*-PPh_2EtPy)Cl]PF_6 (9): A mixture of [{(η^5-C_5Me_5)Rh(μ-Cl)Cl}$_2$] (0.668 g, 1.0 mmol) and PPh_2EtPy (0.291, 1.0 mmol) in methanol (25 mL) was heated under reflux for 8 h. After cooling to room temperature, methanol was removed under reduced pressure to one-fourth its volume and a saturated solution of NH_4PF_6 was added. It gave a red solid, which was recrystallized from CH_2Cl_2/petroleum ether. Yield: 0.542 g, 86%. $C_{29}H_{33}ClF_6NP_2Rh$ (709.88): calcd. C 49.07, H 4.69, N 1.97; found C 49.12, H 4.64, N 1.92. MS (FAB): *m/z* (calcd.) = 564.9 (564) [(η^5-C_5Me_5)Rh(κ^2-*P*-*N*-PPh_2EPyt)Cl], 273.9 (273) [(η^5-C_5Me_5)RhCl]. ^{1}H NMR: δ = 9.56 (dd, *J* = 5.2 Hz, 1 H, py-H6), 7.74–7.72 (m, 5 H, py-H4 + Ph-H2), 7.46–7.32 (m, 6 H, Ph-H3 + -H4), 7.26–7.21 (m, 1 H, py-H5), 7.24 (d, *J* = 7.6 Hz, 1 H, py-H3), 3.22–3.17 (m, 2 H, py-CH_2), 2.41–2.36 (m, 2 H, P-CH_2), 1.51 (s, 15 H, C_5Me_5) ppm. ^{13}C NMR: δ = 8.53 (C-CH_3), 94.72 (C_5Me_5), 159.6 (py-C2), 154.5 (py-C6), 138.4 (CH), 132.5 (CH), 130.3 (Ph-C1), 127.2 (CH), 126.4 (CH), 120.4 (s, CH), 116.3 (s, CH), 37.3 (py-*C*H_2), 28.2 (P-*C*H_2) ppm. ^{31}P{^{1}H} NMR: δ = 10.69 (s, *P*Ph_2EtPy) ppm. IR (KBr pellet): $\tilde{\nu}$ = 1648 (s), 1460 (s), 1440 (m), 1378 (m), 1341 (s), 1245 (m), 1195 (m), 1033 (m), 993 (s), 889 (s), 807 (s), 722 (m), 670 (s), 528 (s), 473 (s) cm^{-1}. UV/Vis: λ (ε, M^{-1}cm^{-1}) = 539 (6310), 487 (12000), 354 (10950), 281 (35090) nm.

[(η^5-C_5Me_5)Ir(κ^2-*P*-*N*-PPh_2EtPy)Cl]PF_6 (10): Prepared by following the procedure for **9** by using [{(η^5-C_5Me_5)Ir(μ-Cl)Cl}$_2$] (0.795 g, 1.0 mmol) instead of [{(η^5-C_5Me_5)Rh(μ-Cl)Cl}$_2$]. Yield: 0.695 g, 78%. $C_{29}H_{33}ClF_6IrNP_2$ (799.20): calcd. C 43.58, H 4.16, N 1.75; found C 43.62, H 4.10, N 1.82. MS (FAB): *m/z* (calcd.) = 654.2 (654) [(η^5-C_5Me_5)Ir(κ^2-*P*-*N*-PPh_2EtPy)Cl], 363.2 (364) [(η^5-C_5Me_5)IrCl]. ^{1}H NMR: δ = 9.56 (dd, *J* = 5.2 Hz, 1 H, py-H6), 7.74–7.72 (m, 5 H, py-H4 + Ph-H2), 7.46–7.32 (m, 6 H, Ph-H3 + -H4), 7.26–7.21 (m, 1 H, py-H5), 7.24 (d, *J* = 7.6 Hz, 1 H, py-H3), 3.22–3.17 (m, 2 H, py-CH_2), 2.41–2.36 (m, 2 H, P-CH_2), 1.56 (s, 15 H, C_5Me_5) ppm. ^{13}C NMR: δ = 8.38 (C-CH_3), 86.69 (C_5Me_5), 162.5 (py-C2), 155.8 (py-C6), 140.5 (CH), 136.6 (CH), 134.6 (Ph-C1), 134.2 (CH), 129.0 (CH), 124.6 (s, CH), 123.2 (s, CH), 35.6 (py-*C*H_2), 26.4 (P-*C*H_2) ppm. ^{31}P{^{1}H} NMR: δ = 2.40 (s, *P*Ph_2EtPy) ppm. IR (KBr pellet): $\tilde{\nu}$ = 1648 (s), 1464 (s), 1434 (m), 1378 (m), 1341 (s), 1245 (m), 1192 (m), 1036 (m), 996 (s), 890 (s), 806 (s), 720

(m), 674 (s), 526 (s), 478 (s) cm^{-1}. UV/Vis: λ (ε, $M^{-1}cm^{-1}$) = 540 (17120), 489 (96560), 357 (94000), 241 (36330) nm.

[(η^5-C_5Me_5)Ir(κ^1-*P*-PPh_2EtPy)(N_3)$_2$] (11): To a solution of complex **10** (0.39 g, 0.5 mmol) in methanol (40 mL) was added sodium azide (0.52 g, 8.0 mmol), and the mixture was stirred at room temperature for 8 h. The resulting solution was evaporated to dryness, and the residue was extracted with dichloromethane and filtered through Celite. The filtrate was saturated with diethyl ether and left undisturbed for slow crystallization. Slowly, it gave a yellow solid, which was filtered, washed with diethyl ether, and dried in air. Yield: 0.30 g, 77% (**11**). $C_{29}H_{33}IrN_7P$ (702.82): calcd. C 49.56, H 4.73, N 13.95; found C 49.60, H 4.75, N 13.92. ^{1}H NMR: δ = 8.56 (d, J = 5.2 Hz, 1 H, py-H6), 7.74–7.72 (m, 5 H, py-H4 + Ph-H2), 7.46–7.32 (m, 6 H, Ph-H3 + -H4), 7.26–7.21 (m, 1 H, py-H5), 7.24 (d, J = 7.6 Hz, 1 H, py-H3), 3.22–3.17 (m, 2 H, py-CH_2), 2.41–2.36 (m, 2 H, P-CH_2), 1.56 (s, 15 H, C_5Me_5) ppm. ^{31}P{^{1}H}NMR: δ = 20.71 (s, *P*Ph_2EtPy) ppm. IR (KBr pellet): $\tilde{\nu}$ = 2024 (s), 1624 (s), 1460 (s), 1432 (m), 1378 (m), 1344 (s), 1235 (m), 1192 (m), 1036 (m), 996 (s), 720 (m), 674 (s), 526 (s), 478 (s) cm^{-1}.

[(η^5-C_5Me_5)Ir(κ^1-*P*-PPh_2EtPy)Cl_2] (12): Prepared by following the procedure for **11** except that NaCl (0.46 g, 8.0 mmol) was used in place of NaN_3. Yield: 0.32 g, 82%. $C_{29}H_{33}Cl_2IrN$ (658.71): calcd. C 52.88, H 5.05, N 2.13; found C 52.85, H 5.08, N 2.18. ^{1}H NMR: δ = 8.46 (d, J = 4.6 Hz, 1 H, py-H6), 7.68–7.71 (m, 5 H, py-H4 + Ph-H2), 7.40–7.30 (m, 6 H, Ph-H3 + -H4), 7.22–7.18 (m, 1 H, py-H5), 7.26 (d, J = 7.7 Hz, 1 H, py-H3), 3.20–3.16 (m, 2 H, py-CH_2), 2.39–2.36 (m, 2 H, P-CH_2), 1.56 (s, 15 H, C_5Me_5) ppm. ^{31}P{^{1}H} NMR: δ = 20.79 (s, PPh_2EtPy) ppm.

Catalytic Experiments: Hydrogen-transfer experiments for the hydrogenation of acetophenone (0.64 mmol) were carried out in water (5 mL) at 80 °C for 8–14 h in the presence of complexes **1**–**10** (6.4 μmol), sodium formate (3.2 mmol), and HCOOH/HCOONa buffer (pH 4.0). The reactions were quenched at 0 °C, and the products were extracted with diethyl ether and separated by silica gel chromatography. These were analyzed by ^{1}H NMR spectroscopy in $CDCl_3$ and the yields of the respective processes were calculated considering relative integral of the ketones and alcohol.

Crystallographic Studies: Suitable crystals for single X-ray diffraction analyses for complexes **1**, **5**, **6**, **9**, and **10** were obtained by slow diffusion of petroleum ether (40–60 °C) into the dichloromethane solution of the respective complexes at room temperature. Preliminary data on the space group and unit-cell dimensions as well as intensity data were collected with an Oxford Diffraction XCAUBER-S′ diffractometer by using graphite monochromated Mo-K_α radiation. The structures were solved by direct methods and refined by using SHELX-97[38] Non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were geometrically fixed and allowed to refine by using a riding model. The computer program PLATON was used for analyzing the interaction and stacking distance.[38] CCDC-742869 (for **1**), -742870 (for **5**), -742871 (for **6**), -742872 (for **10**), and -742873 (for **9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Complex 1: Formula = $C_{42}H_{38}ClNP_2Ru$, M_r = 755.19, triclinic space group $P\bar{1}$, a = 9.423(2) Å, b = 9.704(2) Å, c = 19.907(4) Å, α = 89.961(17)°, β = 78.293(18)°, γ = 71.93(2)°, V = 1690.7(6) Å^3, Z = 2, $D_{calcd.}$ = 1.483 g cm^{-3}, μ = 0.670 mm^{-1}, T = 150(2) K, λ = 0.71073 nm, R(all) = 0.0910, $R[I>2\sigma(I)]$ = 0.0652, wR_2 = 0.2408, $wR_2[I>2\sigma(I)]$ = 0.2353, GooF = 1.050.

Complex 5: Formula = $C_{42}H_{38}BF_4NP_2Ru$, M_r = 806.55, monoclinic space group $P2_1/n$, a = 15.6076(10) Å, b = 10.6738(5) Å, c = 22.571(2) Å, α = 90°, β = 108.903(9)°, γ = 90°, V = 3557.3(4) Å^3, Z = 4, $D_{calcd.}$ = 1.506 g cm^{-3}, μ = 0.585 mm^{-1}, T = 150(2) K, λ = 0.71073 nm, R(all) = 0.0484, $R[I>2\sigma(I)]$ = 0.0373, wR_2 = 0.1026, $wR_2[I>2\sigma(I)]$ = 0.0970, GooF = 1.081.

Complex 6: Formula = $C_{26}H_{26}Cl_3F_6NP_2Ru$, M_r = 735.84, orthorhombic space group $P2_12_12_1$, a = 9.4603(7) Å, b = 11.7153(9) Å, c = 25.822(3) Å, α = 90°, β = 90°, γ = 90°, V = 2861.9(4) Å^3, Z = 4, $D_{calcd.}$ = 1.708 g cm^{-3}, μ = 0.998 mm^{-1}, T = 150(2) K, λ = 0.71073 nm, R(all) = 0.0705, $R[I>2\sigma(I)]$ = 0.0621, wR_2 = 0.1598, $wR_2[I>2\sigma(I)]$ = 0.1571, GooF = 1.111.

Complex 9: Formula = $C_{29}H_{33}ClF_6NP_2Rh$, M_r = 709.86, triclinic space group $P\bar{1}$, a = 8.3137(5) Å, b = 12.0488(8) Å, c = 14.5773(10) Å, α = 96.302(5)°, β = 92.148(5)°, γ = 94.089(5)°, V = 1446.18(16) Å^3, Z = 2, $D_{calcd.}$ = 1.630 g cm^{-3}, μ = 0.853 mm^{-1}, T = 150(2) K, λ = 0.71073 nm, R(all) = 0.0881, $R[I>2\sigma(I)]$ = 0.0753, wR_2 = 0.2127, $wR_2[I>2\sigma(I)]$ = 0.2079, GooF = 1.138.

Complex 10: Formula = $C_{29}H_{33}ClF_6IrNP_2$, M_r = 799.15, triclinic space group $P\bar{1}$, a = 8.3872(2) Å, b = 12.0166(4) Å, c = 14.5758(4) Å, α = 96.887(2)°, β = 91.915(2)°, γ = 93.709(2)°, V = 1454.12(7) Å^3, Z = 2, $D_{calcd.}$ = 1.825 g cm^{-3}, μ = 4.853 mm^{-1}, T = 150(2) K, λ = 0.71073 nm, R(all) = 0.0277, $R[I>2\sigma(I)]$ = 0.0246, wR_2 = 0.0628, $wR_2[I>2\sigma(I)]$ = 0.0621, GooF = 1.082.

Supporting Information (see footnote on the first page of this article): FAB spectra of **1**–**6** and **8**–**10**; cyclic voltammograms of **1** and **2**; π···π interactions in **1**; motifs resulting from various C–H···F weak bonding interactions in **6**; C–H···π interactions in **9**; monohydride inner-sphere mechanism for hydrogen transfer from formic acid to a ketone.

Acknowledgments

We gratefully acknowledge financial support from the Department of Science and Technology, Ministry of Science and Technology, New Delhi, India (Grant No. SR/SI/IC-15/2007). Thanks are also due to Prof. P. Mathur, In-charge, National Single Crystal X-ray Diffraction Facility, Indian Institute of Technology, Mumbai, for providing single-crystal X-ray data. Further, we are grateful to the Head, Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi, for extending laboratory facilities.

[1] a) C. S. Slone, D. A. Weinberger, C. A. Mirkin, *Prog. Inorg. Chem.* **1999**, *48*, 233; b) A. Bader, E. Lindner, *Coord. Chem. Rev.* **1991**, *108*, 27 (hemilabile P,O-donor ligands); c) P. Espinet, K. Soulantica, *Coord. Chem. Rev.* **1999**, *193–195*, 499 (hemilabile P,N-donor ligands); d) P. Braunstein, F. Naud, *Angew. Chem. Int. Ed.* **2001**, *40*, 680 (hemilabile P,N-donor ligands); e) V. V. Grushin, *Organometallics* **2001**, *20*, 3950 and references cited therein.
[2] J. C. Jeffrey, T. B. Rauchfuss, *Inorg. Chem.* **1979**, *18*, 2658.
[3] a) P. Espinet, K. Soulantica, *Coord. Chem. Rev.* **1999**, *195*, 499; b) P. Braunstein, *J. Organomet. Chem.* **2004**, *689*, 3953; c) P. J. Guiry, C. P. Saunders, *Adv. Synth. Catal.* **2004**, *346*, 497; d) A. Pfaltz, W. J. Drury III, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 5723; e) G. Helmchen, A. Pfaltz, *Acc. Chem. Res.* **2000**, *33*, 336.
[4] G. R. Newkome, *Chem. Rev.* **1993**, *93*, 2067.
[5] Z. Z. Zhang, H. Cheng, *Coord. Chem. Rev.* **1996**, *147*, 1.
[6] P. Espinet, K. Soulantica, *Coord. Chem. Rev.* **1998**, *193*, 499.
[7] G. Chelucci, G. Orru, G. A. Pinna, *Tetrahedron* **2003**, *59*, 9471.
[8] a) A. Del Zotto, A. Mezzetti, P. Rigo, *J. Chem. Soc., Dalton Trans.* **1994**, 2257; b) M. P. Anderson, A. L. Casalnuovo, B. J.

Johnson, B. M. Mattson, A. M. Mueting, L. H. Pignolet, *Inorg. Chem.* **1988**, *27*, 1649; c) J. Flapper, H. Kooijman, M. Lutz, A. L. Spek, P. W. N. M. Van Leeuwen, C. J. Elsevier, P. C. J. Kamer, *Organometallics* **2009**, *28*, 1180–1192; d) J. Flapper, H. Kooijman, M. Lutz, A. L. Spek, P. W. N. M. Van Leeuwen, C. J. Elsevier, P. C. J. Kamer, *Organometallics* **2009**, *28*, 3264–3271.

[9] a) E. Drent, P. Arnoldy, P. H. M. Budzelaar, *J. Organomet. Chem.* **1993**, *455*, 247; b) C. S. Consorti, G. Ebeling, J. Dupont, *Tetrahedron Lett.* **2002**, *43*, 753; c) E. Drent, P. Arnoldy, P. H. M. Budzelaar, *J. Organomet. Chem.* **1994**, *475*, 57.

[10] F. Speiser, P. Braunstein, L. Saussine, *Acc. Chem. Res.* **2005**, *38*, 784.

[11] a) S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169; b) V. C. Gibson, S. K. Spitzmesser, *Chem. Rev.* **2003**, *103*, 283.

[12] Q. Jiang, D. Van Plew, S. Murtuza, X. Zhang, *Tetrahedron Lett.* **1996**, *37*, 797.

[13] a) M. A. Bennett, M. I. Bruce, T. W. Matheson, *Comprehensive Organometallic Chemistry* (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon Press, Oxford, UK, **1982**, Ser. 4, p. 796; b) H. Le Bozec, D. Touchard, P. H. Dixneuf, *Adv. Organomet. Chem.* **1989**, *29*, 163; c) M. A. Bennett in *Comprehensive Organometallic Chemistry II* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon Press, Oxford, UK, **1995**, Ser. 7, p. 549; d) E. Wong, C. M. Giandomenico, *Chem. Rev.* **1999**, *99*, 2451; e) C. E. Housecroft in *Comprehensive Coordination Chemistry II* (Eds.: J. A. McCleverty, T. J. Meyer), Pergamon Press, Oxford, UK, **2005**, Ser. 5, p. 555; f) P. Stepnicka, J. Ludvik, J. Canivet, G. Süs-Fink, *Inorg. Chim. Acta* **2006**, *359*, 2369 and references cited therein; g) T. Naota, H. Takaya, S. E. Murahashi, *Chem. Rev.* **1998**, *98*, 2599; h) C. Bruneau, P. H. Dixneuf, *Ruthenium Catalysis and Fine Chemistry*, Springer, Berlin, **2004**, pp. 45.

[14] a) R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, Wiley, Hoboken, NJ, **2005**; b) for highlights of important developments in the metal-ligand cooperative activation of substrates, see: H. Grutzmacher, *Angew. Chem. Int. Ed.* **2008**, *47*, 1814; c) J. Liu, X. Wu, J. A. Iggo, J. Xiao, *Coord. Chem. Rev.* **2008**, *252*, 782; d) K. D. Hesp, R. McDonald, M. J. Ferguson, M. Stradiotto, *J. Am. Chem. Soc.* **2008**, *130*, 16394; e) K. Severin, *Chem. Commun.* **2006**, *31*, 3869.

[15] a) R. Tribo, S. Munoz, J. Pons, R. Yanez, A. Alvarez-Larena, J. F. Piniella, J. Ros, *J. Organomet. Chem.* **2005**, *690*, 4072; b) P. Pelagatti, A. Bacchi, F. Calbiani, M. Carcelli, L. Elviri, C. Pelizzi, D. Rogolino, *J. Organomet. Chem.* **2005**, *690*, 4602; c) J. Dıez, M. P. Gamasa, J. Gimeno, E. Lastra, A. Villar, *Eur. J. Inorg. Chem.* **2006**, *1*, 78; d) W.-M. Cheung, Q.-F. Zhang, I. D. Williams, W.-H. Leung, *Inorg. Chim. Acta* **2006**, *359*, 782; e) Q.-F. Zhang, R. D. Adams, W.-H. Leung, *Inorg. Chim. Acta* **2006**, *359*, 978; f) M. Melchart, A. Habtemariam, S. Parsons, S. A. Moggach, P. J. Sadler, *Inorg. Chim. Acta* **2006**, *359*, 3020; g) F. Csbai, F. Joo, A. M. Trzeciak, J. J. Ziolkowski, *J. Organomet. Chem.* **2006**, *691*, 3371; h) F. Marchetti, C. Pettinari, R. Pettinari, A. Cerquetella, A. Cingolani, E. J. Chan, K. Kozawa, B. W. Skelton, A. H. White, R. Wanke, M. L. Kuznetsov, L. M. D. R. S. Martins, A. J. L. Pombeiro, *Inorg. Chem.* **2007**, *46*, 8245; i) P. Govindaswamy, P. J. Carroll, Y. A. Mozharivskyj, M. R. Kollipara, *J. Organomet. Chem.* **2005**, *690*, 885.

[16] a) C. Joubran, D. B. Grotjahn, J. L. Hubbard, *Organometallics* **1996**, *15*, 1230; b) E. Carmona, A. Cingolani, F. Marchetti, C. Pettinari, R. Pettinari, B. W. Skelton, A. H. White, *Organometallics* **2003**, *22*, 2820; c) T. Steinke, C. Gemel, M. Cokoja, M. Winter, R. A. Fischer, *Chem. Commun.* **2003**, *9*, 1066; d) I. Ara, J. R. Berenguer, E. Eguizabal, J. Fornies, E. Lalinde, A. Martin, *Eur. J. Inorg. Chem.* **2001**, *61*, 631.

[17] a) Y. Sasson, J. Blum, *J. Org. Chem.* **1975**, *40*, 1887; b) R. L. Chowdhury, J. E. Backvall, *J. Chem. Soc., Chem. Commun.* **1991**, 1063; c) D. Muller, G. Umbricht, B. Weber, A. Pfaltz, *Inorg. Chim. Acta* **1991**, *74*, 232; d) S. Gladiali, G. Chelucci, G. Chessa, G. Delogu, F. Soccolini, *J. Organomet. Chem.* **1987**, *327*, C15; e) P. Kvintovics, B. R. James, B. Heil, *J. Chem. Soc., Chem. Commun.* **1986**, 1810; f) S. Gladiali, L. Pinna, G. Delogu, S. de Martin, G. Zassinovich, G. Mestroni, *Tetrahedron: Asymmetry* **1990**, *1*, 635.

[18] a) R. Noyori, M. Yamakawa, S. Hashiguchi, *J. Org. Chem.* **2001**, *66*, 7931; b) A. J. Blacker, B. J. Mellor (Zeneca Ltd.), WO9842643, **1998**.

[19] a) A. Singh, N. Singh, D. S. Pandey, *J. Organomet. Chem.* **2002**, *642*, 48; b) M. Chandra, A. N. Sahay, S. M. Mobin, D. S. Pandey, *J. Organomet. Chem.* **2002**, *658*, 43.

[20] a) P. Govindaswamy, Y. A. Mozharivskyj, M. R. Kollipara, *Polyhedron* **2007**, *26*, 5039–5044; b) P. Govindaswamy, Y. A. Mozharivskyj, M. R. Kollipara, *Polyhedron* **2005**, *24*, 1710; c) M. A. Rida, C. Coperet, A. K. Smith, *J. Organomet. Chem.* **2001**, *628*, 1–10.

[21] a) M. Chandra, A. N. Sahay, D. S. Pandey, R. P. Tripathi, J. K. Saxena, V. J. M. Reddy, M. C. Puerta, P. Valerga, *J. Organomet. Chem.* **2004**, *689*, 2256; b) W. J. Perez, C. H. Lake, R. F. See, L. M. Toomey, M. R. Churchill, K. J. Takeuchi, C. P. Radano, W. J. Boyko, C. A. Bessel, *J. Chem. Soc., Dalton Trans.* **1999**, 2281.

[22] a) M. R. Churchill, K. M. Keil, F. V. Bright, S. Pandey, G. A. Baker, J. B. Keister, *Inorg. Chem.* **2000**, *39*, 5807; b) P. Ghosh, A. Chakravorty, *Inorg. Chem.* **1997**, *36*, 64.

[23] P. Paul, B. Tyagi, A. K. Bilakhia, P. Dastidar, E. Suresh, *Inorg. Chem.* **2000**, *39*, 14.

[24] P. Govindaswamy, J. Canivet, B. Therrien, G. Suss-Fink, P. Stepnicka, J. Ludvik, *J. Organomet. Chem.* **2007**, *692*, 3664.

[25] a) C. D. Nunes, M. Pillinger, A. Hazell, J. Jepsen, T. M. Santos, J. Madureira, A. D. Lopes, I. S. Goncalves, *Polyhedron* **2003**, *22*, 2799; b) A. Singh, A. K. Singh, M. Trivedi, D. S. Pandey, *J. Organomet. Chem.* **2005**, *690*, 4243–4251.

[26] a) P. Kopel, Z. Travnicek, L. Kvitek, R. Panchartkova, M. Biler, M. Marek, M. Nadvornik, *Polyhedron* **1999**, *18*, 1779; b) S. Kar, T. A. Millar, S. Chakraborty, B. Sarkar, B. Pradhan, R. K. Singh, T. Kunda, M. D. Ward, G. K. Lahiri, *Dalton Trans.* **2003**, 2591.

[27] J. H. Palmer, M. W. Day, A. W. Wilson, L. M. Henling, Z. Gross, H. B. Gray, *J. Am. Chem. Soc.* **2008**, *130*, 7786–7787.

[28] A. Comas-Vives, G. Ujaque, A. Lledós, *Organometallics* **2007**, *26*, 4135.

[29] T. Li, R. Churlaud, A. J. Lough, K. Abdur-Rashid, R. H. Morris, *Organometallics* **2004**, *23*, 6239.

[30] For selected recent reviews, see: a) T. Ikariya, A. J. Blacker, *Acc. Chem. Res.* **2007**, *40*, 1300; b) X. Wu, J. L. Xiao, *Chem. Commun.* **2007**, 2449; c) S. Gladiali, E. Alberico, *Chem. Soc. Rev.* **2006**, *35*, 226; d) J. S. M. Samec, J.-E. Bäckvall, P. G. Andersson, P. Brandt, *Chem. Soc. Rev.* **2006**, *35*, 237; e) S. E. Clapham, A. Hadzovic, R. H. Morris, *Coord. Chem. Rev.* **2004**, *248*, 2201; f) K. Everaere, A. Mortreux, J.-F. Carpentier, *Adv. Synth. Catal.* **2003**, *345*, 67; g) M. J. Palmer, M. Wills, *Tetrahedron: Asymmetry* **1999**, *10*, 2045; h) R. Noyori, S. Hashiguchi, *Acc. Chem. Res.* **1997**, *30*, 97.

[31] M. T. Reetz, X. G. Li, *J. Am. Chem. Soc.* **2006**, *128*, 1044.

[32] a) C. P. Casey, T. B. Clark, I. A. Guzei, *J. Am. Chem. Soc.* **2007**, *129*, 11821; b) H. Guan, M. Iimura, M. P. Magee, J. R. Norton, G. Zhu, *J. Am. Chem. Soc.* **2005**, *127*, 7805; c) R. L. Chowdhury, J.-E. Bäckvall, *J. Chem. Soc., Chem. Commun.* **1991**, 1063; d) A. Aranyos, G. Csjernyik, K. J. Szabo, J.-E. Bäckvall, *Chem. Commun.* **1999**, 351.

[33] B. J. Dunne, R. B. Morris, A. G. Orpen, *J. Chem. Soc., Dalton Trans.* **1991**, 653.

[34] D. D. Perrin, W. L. F. Armango, D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon, Oxford, UK, **1986**.

[35] M. I. Bruce, C. Hameister, A. G. Swincer, R. C. Wallis, *Inorg. Synth.* **1982**, *21*, 78.

[36] a) M. A. Bennett, A. K. Smith, *J. Chem. Soc., Dalton Trans.* **1974**, 233–241; b) M. A. Bennett, T. N. Huang, T. W. Matheson, A. K. Smith, *Inorg. Synth.* **1982**, *21*, 74.

[37] a) W. Kang, K. Moseley, P. M. Maitlis, *J. Am. Chem. Soc.* **1969**, *91*, 5970; b) R. G. Ball, W. A. G. Graham, D. M. Heinekey, J. K. Hoyano, A. D. McMaster, B. M. Mattson, S. T. Michel, *Inorg. Chem.* **1990**, *29*, 2023; c) C. White, A. Yates, P. M. Maitlis, *Inorg. Synth.* **1992**, *29*, 228.
[38] a) S. Mackay, W. Dong, C. Edwards, A. Henderson, C. Gilmox, N. Stewart, K. Shankland, A. Donald, University of Glasgow, Scotland, **1999**; b) G. M. Sheldrick, *SHELX-97: Program for Refinement of crystal Structures*, University of Gottingen, Gottingen, Germany, **1997**; c) *PLATON*: A. L. Spek, *Acta Crystallogr., Sect. A* **1990**, *46*, C31.

Received: October 14, 2009
Published Online: December 22, 2009

