The Anion of a Phenyltris(alkylamino)phosphonium (PhTAP) Salt as a Chelating Ligand: Synthesis and X-ray Crystal Structure of a 16-Electron Ruthenium(II) Organometallic Complex

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The phosphonium salt $[PhP(NH^iPr)_3]Br$ has been synthesized, and the ligand properties of its deprotonated forms have been investigated. Treatment of its dilithiate $Li_2[PhP(N^iPr)_3]$ with the dimer $[(\eta\text{-}p\text{-cymene})RuCl_2]_2$ provides the unsaturated 16-electron cation $[(\eta\text{-}p\text{-cymene})Ru\{\eta^2\text{-}(^iPrN)_2PPh(NH^iPr)\}]^+$ which adds cyanide and carbon monoxide (reversibly) and has been structurally characterized as its tetraphenylborate salt.

The chemistry of complexes containing tripod ligands continues to provide new and exciting examples of structure and reactivity in coordination and organometallic chemistry.[1] The ability of a tripod ligand to effectively provide a coordination pocket to encapsulate a metal center allows both the steric shielding of the remaining coordination sites at the metal and a strict control over the stereochemistry of these sites, which may be finely adjusted by choice of donor atom substituent(s). The implications of orders of rotational symmetry higher than two for controlling the stereochemistry of ligand transformations in stoichiometric and catalytic processes has recently been attracting increasing attention.[2] Our interest in developing new ligands for asymmetric catalysis by octahedral metal complexes has lead us to consider ways in which tripod ligands may be used to reduce their symmetry to C_3 and thus
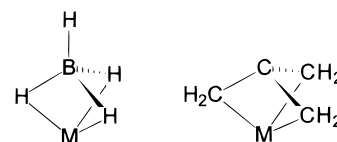

Figure 1.

provide three homotopic coordination sites for substrate coordination opposite the ligand.[3]

The majority of tripodal ligands contain a bridgehead atom linked to the three donor atoms via mono- or diatomic arms. However, systems which may be regarded as a third structural type in which the three donor atoms are directly bonded to the bridgehead only rarely behave as tripodal ligands. Perhaps the best known examples of this type of coordination are tetrahydroborate, which is known to coordinate in an η^3-mode in complexes such as $[M(BH_4)_4]$ (M = Zr, Hf),[4] and the trimethylenemethane (TMM) ligand $[C(CH_2)_3]^{2-}$, which commonly occurs in an η^4-coordination mode and may be included in this category (Figure 1).[5] Some time ago we recognized that such tripodal ligands, possessing approximately tetrahedral donor atoms bearing one bulky substituent, could be effective in the role we have identified since the two possible arrangements of the substituents around the coordinated ligand would provide the required chiral complexes with C_3 symmetry (Figure 2). Furthermore, the anticipated rigidity of such a metal−ligand unit and the proximity of the stereogenic centers to the catalytically active site are expected to provide effective stereocontrol over processes occurring at the metal center.

With the aim of developing a new ligand system of this type, we have recently been considering the system

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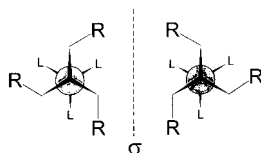(5) Jones, M. D.; Kemmitt, R. D. W. *Adv. Organomet. Chem.* **1987**, *27*, 279.

Figure 2. Formation of C_3-symmetric octahedral complexes by tripod ligands in which the donor atoms are directly bonded to the bridgehead atom.

$[C(NR)_3]^{2-}$ as an isoelectronic analogue of the TMM ligand.[3,6] However, although we have found 1,2,3-substituted guanidines and their anions to be flexible monodentate,[7] chelating,[8] and bridging ligands,[9] we have yet to observe the desired tripodal coordination of all three nitrogen atoms to a single metal. Given the strong preference of the TMM ligand to adopt this coordination mode,[10] we were initially unsure of the reasons for this difference in behavior. However, we now consider the situation to be a result principally of the geometric changes in the metal–ligand system brought about by substituting carbon by nitrogen.[11] On coordination to a metal center, the planar, "cross-conjugated" TMM dianion undergoes a so-called "umbrella" distortion in which the ligand typically distorts by 12° from planarity toward the metal.[12] This distortion clearly involves a loss of conjugation across the ligand. The apparent absence of an equivalent coordination mode of the $[C(NR)_3]^{2-}$ ligand suggests that the energy gained by M–L bond formation is insufficient to compensate for the distortion involved in coordination of the ligand. The smaller size of nitrogen compared to carbon means that, for a given metal, the distortion from planarity required for η^3-coordination of a $C(N)_3$ ligand is greater than that for a $C(C)_3$ ligand. Coupled with the stability of the η^2-chelating coordination mode, which contrasts with the rarity of a similar mode for the TMM ligand, we believe that it is this factor which accounts for the failure of the $[C(NR)_3]^{2-}$ ligand to adopt our desired η^3-tripodal coordination.

Recognition of these problems with TMM analogues has lead us to consider ligands based on tetrahedral systems. Such ligands should avoid the problems associated with ligand distortion on coordination since they effectively have the above distortion built in. We have identified the dianions $[PhP(NR)_3]^{2-}$, derived by the triple deprotonation of the phenyltris(alkylamino)phosphonium (PhTAP) cations $[PhP(NHR)_3]^+$, as possible ligands fulfilling these criteria, and here we report

an investigation of the coordination of such a ligand with a ruthenium(II) arene fragment.

Results and Discussion

The phosphonium salt $[PhP(NH^iPr)_3]Br$ was synthesised by the *in-situ* preparation of $[PhPBrCl_2]Br$ from $PhPCl_2$ followed by its condensation with isopropylamine.[13] The crystalline salt was pure by elemental analysis and NMR (^1H, ^{13}C, and ^{31}P), and these data closely correspond to those previously reported; however, its melting point of 215 °C differs very significantly from the published value of 138–140 °C.[13,14] Treatment of the finely ground salt in THF (in which it is largely insoluble) with 3 mol equiv of *n*-butyllithium provides a yellow solution which, when treated with 3 mol equiv of MeI, provided the trimethylated phosphonium cation $[PhP\{N(Me)^iPr\}_3]^+$.[15] Furthermore, it was established that the starting salt $[PhP(NH^iPr)_3]Br$ remained unchanged on treatment with MeI under the same conditions. These observations, therefore, strongly suggest that the yellow solution contains the dilithiate $Li_2[PhP(N^iPr)_3]$, which was used in subsequent reactions without further characterization.

In an attempt to prepare a complex of the new ligand coordinated through all three nitrogen atoms the dimer $[(\eta\text{-}p\text{-cymene})RuCl_2]_2$ was treated with 2 mol equiv of the PhTAP dianion, which gave a dark blue/green solution of a product to which we assign the formula $[(\eta\text{-}p\text{-cymene})Ru\{(^iPrN)_3PPh\}]$ (**1**). Despite careful exclusion of air, it proved very difficult to isolate this product uncontaminated by its deep purple decomposition product $[(\eta\text{-}p\text{-cymene})Ru\{\eta^2\text{-}(^iPrN)_2PPh(NH^iPr)\}]^+$ (**2**). In the absence of a clean sample of the primary product, we have, therefore, characterized this stable complex. We were initially unsure whether the decomposition was due to oxidation or hydrolysis; however, cyclic voltametry of the cationic purple product, isolated as its tetraphenylborate salt, failed to reveal a reduction process at a potential characteristic for a Ru(III)/Ru(II) couple, but rather a reduction wave at -1.66 V *vs* ferrocene was observed which we assign to a Ru(II)/Ru(I) couple. We, therefore, conclude that neutral **1** is strongly basic and that the formation of the cationic deep purple product **2** is due to protonation by water. This is further confirmed by the observation that the deep blue/green color of **1** is regenerated by treatment of **2** with *n*-butyllithium in THF solution. That the purple **2** contained Ru(II) was confirmed by the observation of a sharp unshifted ^1H NMR spectrum which showed, in addition to signals due to the aromatic groups present, the presence of three independent isopropyl groups on the ligand and a signal at 2.97 ppm which may be assigned to an N–H proton. These data, therefore, suggest a complex containing the ligand as a

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(14) The phosphonium salt $[PPh(NH^iPr)_3]Br$ has been crystallographically characterized (monoclinic, space group $C2/c$, $a = 14.485$-(3) Å, $b = 9.213(3)$ Å, $c = 29.213(5)$ Å; $\beta = 99.24(2)°$, R1 = 0.0531) and full details are provided in the Supporting Information.

(15) $[PhP\{N(Me)^iPr\}_3]I$: ^1H NMR (250 MHz, CDCl$_3$, 20 °C, TMS) δ = 7.7 (mult, 5H, Ph), 3.5 (mult, 3H, ^iPr–CH), 2.72 (d, $J_{P-H} = 12$ Hz, 9H, CH_3), 1.22 (d, $J = 9$ Hz, 18H, ^iPr-CH$_3$); MS (+ FAB) *m/z* 324 (100) [M$^+$].
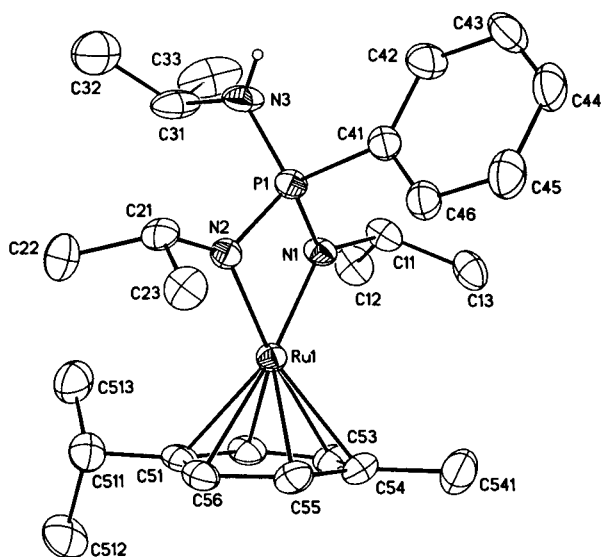
Figure 3. Thermal ellipsoid plot of the structure of the cation in [(η-p-cymene)Ru{η^2-(^{i}PrN)$_2$PPh(NH^{i}Pr)}][BPh$_4$] (**2**).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Cation in [(η-p-cymene)Ru{η^2-(^{i}PrN)$_2$PPh(NH^{i}Pr)}][BPh$_4$] (2)

N1−Ru	2.011(3)	P−N1−Ru	96.10(14)
N2−Ru	2.017(3)	P−N2−Ru	96.26(13)
P−N1	1.620(3)	N1−P−N3	115.6(2)
P−N2	1.608(3)	N2−P−N3	115.7(2)
P−N3	1.616(3)	N1−P−C41	113.5(2)
P−C41	1.801(3)	N2−P−C41	113.6(2)
N1−C11	1.477(4)	N3−P−C41	104.8(2)
N2−C21	1.476(4)	P−N1−C11	124.0(2)
N3−C31	1.480(5)	P−N2−C21	125.8(2)
N1−Ru−N2	71.76(11)	P−N3−C31	122.9(3)
N1−P−N2	94.01(14)	P−N1−Ru−N2	13.9(3)

monoanion with the third nitrogen present as an −NH^{i}Pr group. Whether this third nitrogen is bonded to the metal is unclear, however, in the absence of such coordination, a 16-electron Ru(II) complex results. The fact that the complex is a cation precludes the presence of a further anionic ligand, and since there is no evidence in the NMR spectrum for any other organic group which may be coordinated to the metal and the FAB mass spectrum shows a molecular ion at $m/z =$ 517 consistent with the formulation of the complex as [(η-p-cymene)Ru{(^{i}PrN)$_2$(NH^{i}Pr)PPh}]$^+$, it appears that **2** is either an unusual example of a 16-electron Ru(II) organometallic complex or contains the monoanionic ligand in the desired η^3-coordination mode.

An X-ray crystal structure analysis of **2**[BPh$_4$] shows that it is in fact a 16-electron complex with the ligand in an η^2-chelating coordination mode with the −NH^{i}Pr group remaining uncoordinated. Apart from the η-bonded p-cymene, no other ligands are present. A thermal ellipsoid plot of the structure of **2** is shown in Figure 3, and significant bond lengths and angles are given in Table 1. The two Ru−N bond distances do not differ significantly (2.017(3) and 2.011(3) Å), and the P−N bond distances are also not significantly different, with the bond to the uncoordinated nitrogen N(3) (1.616(3) Å) perhaps surprisingly lying between the values for the two coordinated nitrogens (1.608(3) and 1.620(3) Å). The chelating angle at Ru (N(1)−Ru−N(2)) is 71.76(11)°, which compares with a value of 62.07(7)° for the
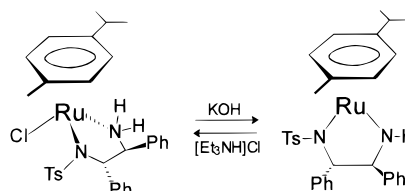
corresponding N−Ru−N angle in the complex containing the chelating guanidine monoanion [(η-p-cymene)-Ru{η^2-(^{i}PrN)$_2$C(NH^{i}Pr)}Cl],[16] the difference attributable to the larger size of phosphorus. The angle N(1)−P−N(2) is distorted by *ca.* 15° from tetrahedral (94.01(14)°), while the remaining angles at P are correspondingly expanded. The puckering of the N(1)−P−N(2)−Ru plane is slight [13.9(3)°] but not negligible, indicating the possibility of a small *pseudo* π-allyl contribution to the M−L bonding, although the Ru−P separation of 2.71 Å suggests that this is unlikely to be significant. The angle between the planes defined by the p-cymene ring and the atoms N(1), Ru(1), and N(2) is 91.0°, indicating negligible pyramidalization of the ruthenium center, consistent with the PhTAP ligand acting as a π-donor.[17]

Although **2** is an unusual example of a 16-electron Ru(II) complex containing an η-bonded arene ligand, it is not unique, and a comparison with the other known example of such a system is of interest. Noyori has found that KOH treatment of the system [(η-p-cymene)-Ru{(S,S)-TsDPEN}Cl] ((S,S)-TsDPEN = (1S,2S)-N-p-toluenesulphonyl-1,2-diphenylethylenediamine) results in elimination of one of the acidic NH$_2$ protons and the Cl$^-$ ligand and formation of a stable neutral 16-electron species, which is also deep purple in color.[18] This process may be reversed by treatment with triethylammonium chloride (Scheme 1). The 16-electron complex is a highly effective catalyst for the asymmetric transfer hydrogenation of ketones and is readily converted into the yellow active hydrido species by treatment with isopropyl alcohol, the reducing agent used in this process. In contrast to these observations, **2** is unaffected by treatment with sources of chloride (PPh$_4$Cl) or HCl (NEt$_3$HCl). It would, therefore, appear that the PhTAP-derived chelating ligand is more effective at stabilizing the ruthenium unsaturation by π-donation from the coordinated amido nitrogen atoms than is the TsDPEN ligand. This is perhaps as would be predicted if the amido substituents in the two ligand systems are compared. The resulting increased electron density at the ruthenium in **2** is illustrated by its reactivity with π-acceptor ligands. Passing a stream of carbon monoxide through a CH$_2$Cl$_2$ solution of **2** leads to the rapid bleaching of the purple color of the solution to yellow. This solution shows a sharp absorption in the infrared at 1993 cm^{-1} attributable to the coordinated CO ligand, a surprisingly low frequency for a cationic complex, and a further illustration of the strong π-donor character of the PhTAP-derived ligand. Allowing this solution to

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stand under a nitrogen atmosphere leads to rapid regeneration of the purple color, and within 10 min at room temperature, the IR absorption of the CO complex has disappeared. Attempted crystallization of the CO complex under an atmosphere of CO led to slow conversion to secondary products which could be followed by ^{31}P NMR, a total of six signals being observed after a period of 1 week. In an attempt to prepare a stable derivative of **2**, the coordination of various other π-acceptor ligands was investigated. Both triphenylphosphine and triphenyl phosphite remained uncoordinated, although it is reasonable to assume that the bulk of the PhTAP ligand might be responsible for this. However, treatment of a methanol solution of **2** with potassium cyanide instantly gave a stable yellow solution displaying a sharp $\nu(C\equiv N)$ mode at 2102 cm^{-1}. A single signal at 34.6 ppm in the ^{31}P NMR spectrum of this solution showed it to be uncontaminated by other products. The high solubility of this neutral complex in all solvents has so far prevented us from obtaining crystals suitable for crystallography. The stability of this cyanide complex compared with that of CO is perhaps unsurprising given the involatile nature of the ligand, however, it is probable that the additional ionic component of the M–CN bond adds to the stability. The donor strength of the PhTAP ligand is further indicated by the low value of the C≡N stretching frequency, which is due to considerable back-bonding from the metal and, thus, indicates high electron density at the metal in **2**. In contrast to Noyori's complex, **2** shows no reactivity toward isopropyl alcohol or, taking account of the difference in charge between the two complexes, sodium isopropoxide. This may presumably be attributed to the electronic differences between the two complexes, although, as noted above, steric effects may be significant in **2**.

To our knowledge there have been only two previous reports of complexes containing ligands of the general type [RP(NR′)$_2$NR′$_2$]$^-$, although in both of these cases the ligand was derived from an aminobis(imino)phosphorane [(NR)$_2$PNR$_2$] and not from a phosphonium salt. The complex [(η^3-C$_3$H$_5$)Ni{η^2-RP(NR′)$_2$NR′$_2$}]$^-$, (R = allyl, R′ = SiMe$_3$) has been shown to be an effective catalyst for ethene[19] and 1-alkene[20] polymerization, and its palladium analogue has been structurally characterized.[19] However, in the current context, the behavior of the complexes [(CO)$_n$Mn{η^2-RP(NR′)$_2$NR′$_2$}]$^-$ (R = Br, R′ = SiMe$_3$, n = 3, 4; R = OPh, R′ = SiMe$_3$, n = 3) are of greater interest.[21] The tetracarbonyl complex with R = Br shows a reversible loss of a carbonyl ligand generating a 16-electron Mn(I) species, while substitution of Br by phenoxide provides a tricarbonyl complex which shows no tendency to coordinate CO to attain an 18-electron configuration. The ability of these ligands to stabilize formally unsaturated species has, therefore, been observed previously, and it would seem that such behavior could develop into a general feature of their chemistry. There is a clear relationship between these ligands and the extensively studied phosphoniobis-

(methanide) ligands [R$_2$P(CH$_2$)$_2$]$^-$.[22] However, no tendency for these ligands to stabilize formally unsaturated metal complexes has been noted, and this is presumably a reflection of the absence of electrons in π-symmetry orbitals on the carbon donor atoms.

The question of whether the ligand dianions [Ph(NR)$_3$]$^{2-}$ are capable of displaying an η^3-coordination mode as we wish still remains to be answered. Clearly, in the present case, what we assume to be the neutral complex [(η-p-cymene)Ru{(^{i}PrN)$_3$PPh}] (**1**) may contain the ligand in an η^2- or η^3-mode. If the third nitrogen is coordinated, its high basicity suggests that its interaction with the metal is not strong and the available evidence would seem to suggest that it is in fact uncoordinated. Whether this is due to electronic or steric effects is a moot point, however, inspection of molecular models suggests that it is possible that excessive steric interaction between the isopropyl groups on the ligand and the alkyl groups on the η-bonded arene could prevent coordination of the third nitrogen.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of dry, oxygen-free nitrogen using standard Schlenk techniques and solvents which were distilled from the appropriate drying agents under nitrogen immediately prior to use. The dimer [(η-p-cymene)RuCl$_2$]$_2$ was prepared according to the literature,[23] while the phosphonium salt [PhP(NH^{i}Pr)$_3$]Br was prepared by modification of a literature procedure as described below.[13] NMR spectra were recorded on a Bruker AC 250 spectrometer, mass spectra on a Kratos MS50 TC instrument in positive-ion FAB mode using 3-nitrobenzyl alcohol as the matrix and CsI as calibrant, and infrared spectra on a Perkin-Elmer Paragon instrument. Electrochemical measurements were performed using GPES, version 4, software run on a personal computer connected to an Antilab system via an PSTAT 10 potentiostat. Cyclic voltammetry was performed using a standard three-electrode configuration with platinum working (0.5 mm diameter disc) and counter electrodes and a Ag/AgCl reference electrode, which gave the CpFe/CpFe$^+$ couple at 0.58 V. All measurements were made in a nitrogen-purged solution of CH$_2$Cl$_2$/0.5M [n-Bu$_4$N][BF$_4$].

Preparation of [PhP(NH^{i}Pr)$_3$]Br. To a 500 cm^3 round-bottomed flask fitted with a reflux condenser and a pressure equalizing dropping funnel was added a solution containing 5 cm^3 of PPhCl$_2$ (6.59 g, 36.8 mmol) in 100 cm^3 of CHCl$_3$. To this solution was added dropwise a solution of 1.89 cm^3 of Br$_2$ (5.89 g, 36.8 mmol) in 20 cm^3 of CHCl$_3$. The resulting bright yellow precipitate of [PhPCl$_2$Br]Br was allowed to stir for 30 min, and then a solution containing 19 cm^3 of isopropylamine (13.19 g, 0.223 mol) in 100 cm^3 of CHCl$_3$ was added dropwise over a period of 30 min. As the exothermic reaction proceeded, the precipitate dissolved to give a yellow solution which became colorless once all of the amine had been added. The resulting solution was finally heated to reflux for 2 h. Separation of the product from isopropylammonium bromide was achieved by column chromatography on silica, eluting with CHCl$_3$/CH$_3$OH (3:1). Crystallization of the product from MeCN provided 6.3 g of large colorless crystals (47%).[14] M.p: 215 °C. Anal. Calcd for C$_{15}$H$_{29}$BrN$_3$P: C, 49.7; H, 8.01; N, 11.6. Found: C, 51.1; H, 8.35; N, 11.85. ^{1}H NMR (250 MHz, CDCl$_3$, 20 °C, TMS): δ 8.1 (mult, 2H, Ph), 7.45 (mult, 3H, Ph), 5.43

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(dd, J_{H-H} = 9.8 Hz, J_{P-H} = 15.5 Hz, 3H, NH), 3.30 (mult, 3H, CH), 1.10 (d, 18H, CH$_3$). ^{13}C{^{1}H} NMR (62.9 MHz, CDCl$_3$, 20 °C, TMS): δ 132.9 (d, J_{P-C} = 2.8 Hz), 132.3 (d, J_{P-C} = 11.3 Hz), 128.6 (d, J_{P-C} = 14 Hz), 126.0 (d, J_{P-C} = 144 Hz), 42.7 (s), 24.55 (s). ^{31}P NMR (101.2 MHz, CDCl$_3$, 20 °C, H$_3$PO$_4$): δ 29.7. MS (+ FAB): m/z: 281 (100) [M$^+$], 223 (30) [M$^+$ − NH^{i}Pr], 166 (31) [M$^+$ − 2NH^{i}Pr].

Preparation of [(η-p-cymene)Ru{η^2-(^{i}PrN)$_2$PPh-(NH^{i}Pr)}][BPh$_4$]. To a suspension of 454 mg of finely ground [PhP(NH^{i}Pr)$_3$]Br (1.25 mmol) in THF (30 cm^3) at −78 °C was added 1.5 cm^3 of a 2.5 M solution of n-BuLi in hexane (3.75 mmol). On warming to room temperature, the salt dissolved and a pale yellow solution was formed. The solution was stirred at room temperature for a further 15 min and recooled to −78 °C. To the solution was added 380 mg of [(η-p-cymene)-RuCl$_2$]$_2$ (0.621 mmol), and the mixture was allowed to warm to room temperature and stir for 1 h. The solvent was removed from the resulting deep blue/green solution under vacuum, and the residue was dissolved in wet methanol, resulting in a deep purple solution to which 450 mg of NaBPh$_4$ (1.32 mmol) was added. After the mixture was stirred for 30 min, the methanol was removed under vacuum and the residue was washed with ether (2 × 10 cm^3) to remove the last traces of methanol. The residue was dissolved in CH$_2$Cl$_2$ (5 cm^3), and the solution was passed through a short (10 cm) column of silica by eluting with CH$_2$Cl$_2$. The deep purple band was collected, the solvent removed under vacuum, and the product crystallized from hot methanol to yield 671 mg (64%) of purple/black crystals in three crops. Anal. Calcd for C$_{49}$H$_{61}$BN$_3$PRu: C, 70.7; H, 7.09; N, 5.05. Found: C, 71.1; H, 7.25; N, 4.99. ^{1}H NMR (250 MHz, CDCl$_3$, 20 °C, TMS): δ 7.6−6.8 (mult, 25H, Ph), 5.55 (mult, (AB)$_2$, J_{A-B} = 6.3 Hz, 4H, arene-CH), 3.45 (sept, J = 6.8 Hz, 1H, CH), 3.31 (sept, J = 6.8 Hz, 1H, CH), 2.97 (s, br, 1H, NH), 2.91 (sept, J = 5.9 Hz, 1H, CH), 2.50 (sept, J = 6.3 Hz, 1H, CH), 1.93 (s, 3H, arene-CH), 1.31 (d, J = 6.8 Hz, 6H, ^{i}Pr-CH$_3$), 1.30 (d, J = 6.8 Hz, 6H, ^{i}Pr-CH$_3$), 1.07 (d, J = 5.9 Hz, 6H, ^{i}Pr-CH$_3$), 1.01 (d, J = 6.3 Hz, 6H, ^{i}Pr-CH$_3$). ^{13}C{^{1}H} NMR (62.9 MHz, CDCl$_3$, 20 °C, TMS): δ 164.4 (d, J_{B-C} = 8.2 Hz, B−Ph), 136.2 (B−Ph), 133.1 (d, J_{P-C} = 2.9 Hz, Ph), 130.2 (d, J_{P-C} = 9.8 Hz, Ph), 129.2 (d, J_{P-C} = 12.1 Hz, Ph), 127.0 (Ph), 125.3 (q, J_{B-C} = 2.6 Hz, B−Ph), 121.5 (B−Ph), 96.8 (Ar-CH), 84.8 (Ar-CH), 81.7 (Ar−CH), 79.5 (Ar-CH), 47.47 (^{i}Pr−CH), 47.42 (^{i}Pr-CH), 431.7 (^{i}Pr-CH), 26.3 (d, J_{P-C} = 9.3 Hz, ^{i}Pr-CH$_3$), 25.7 (d, J_{P-C} = 4.6 Hz, ^{i}Pr-CH$_3$), 25.1 (d, J_{P-C} = 3.9 Hz, ^{i}Pr-CH$_3$), 20.2 (Ar-CH$_3$, ^{i}Pr−CH$_3$), 15.1 (Ar-CH$_3$, ^{i}Pr-CH$_3$). ^{31}P NMR (101.2 MHz, CDCl$_3$, 20 °C, H$_3$PO$_4$): δ 49.6. MS (+ FAB): m/z 517 (23) [M$^+$], 281 (100) [M$^+$ − Ru(p-cymene)].

Reaction of [(η-p-cymene)Ru{η^2-(^{i}PrN)$_2$PPh(NH^{i}Pr)}]-[BPh$_4$] (2) with CO. A slow stream of CO was passed through a deep purple solution containing 150 mg (0.18 mmol) of **2** in 20 cm^3 of CH$_2$Cl$_2$. Within 30 s the solution had changed color to pale yellow. The solution was stable under an atmosphere of CO, but under nitrogen it reverted back to the deep purple color over a period of 10 min, and this cycle could be repeated. The infrared spectrum of the yellow solution showed a strong absorption at 1993 cm^{-1}. Characterization of this species was hampered by its decomposition to further products over longer periods under a CO atmosphere.

Reaction of [(η-p-cymene)Ru{η^2-(^{i}PrN)$_2$PPh(NH^{i}Pr)}]-[BPh$_4$] (2) with CN$^-$. To a solution containing **2** (150 mg, 0.18 mmol) in 20 cm^3 of methanol was added KCN (13 mg, 0.019 mmol). The solution rapidly changed color to bright

yellow, and after 1 h of stirring, the solvent was removed in vacuum. Extraction of the residue with pentane gave a bright yellow solution from which only an oil could be obtained by concentration and cooling. IR (pentane): ν(C≡N) 2102 cm^{-1}. ^{1}H NMR (250 MHz, CDCl$_3$, 20 °C, TMS): δ 7.8 (m, 2H, Ph), 7.4 (m, 3H, Ph), 5.2 (m, 4H, Ar-CH), 3.9 (br, 1H, NH), 3.32 (sept, J = 8.6 Hz, 1H, ^{i}Pr-CH), 3.23 (sept, J = 7.9 Hz, 1H, ^{i}Pr-CH), 2.96 (sept, J = 7.8 Hz, 1H, ^{i}Pr-CH), 2.76 (sept, J = 7.8 Hz, 1H, ^{i}Pr-CH), 2.15 (s, 3H, arene-CH$_3$), 1.21 (d, J = 8.6 Hz, 6H, ^{i}Pr-CH$_3$), 1.12 (d, J = 7.9 Hz, 6H, ^{i}Pr-CH$_3$), 1.04 (d, J = 7.8 Hz, 6H, ^{i}Pr-CH$_3$), 0.93 (d, J = 7.8 Hz, 6H, ^{i}Pr-CH$_3$). ^{31}P NMR (101.2 MHz, CDCl$_3$, 20 °C, H$_3$PO$_4$): δ 34.6. MS (+ FAB): m/z 543 (100) [M$^+$], 517 (84) [M$^+$ − CN], 280 (43) [M$^+$ − CN − {Ru(p-cymene)}].

X-ray Crystallography. Crystals of **2** were grown from a saturated methanol solution by slow cooling to −20 °C. *Crystal data.* C$_{49}$H$_{61}$BN$_3$PRu, M = 834.86, monoclinic, a = 9.897(2) Å, b = 28.024(5) Å, c = 16.213(3) Å, β = 102.86(2)°, V = 4383.9-(14) Å^3 (from 48 reflections, 14° < θ < 15° measured at ±ω, λ = 0.710 73 Å), space group $P2_1/n$, Z = 4, D_c = 1.265 g cm^{-3}, $F(000)$ = 1760, purple lath, 0.51 × 0.27 × 0.12 mm^3, T = 150-(2) K, μ(Mo Kα) = 0.430 mm^{-1}. Intensity data were collected in the range 5° < 2θ < 50° using $\omega\theta$ scans with on-line profile fitting[24] on a Stoe Stadi-4 diffractometer equipped with an Oxford Cryosystems low-temperature device.[25] Following data reduction and the application of an absorption correction based on φ-scans (T_{min} = 0.438; T_{max} = 0.480), the structure was solved by direct methods (SIR92)[26] and refined by full-matrix least-squares against F^2 (SHELXTL).[27] H atoms attached to C were placed in calculated positions and subsequently allowed to ride on their parent atoms; the H atom attached to N3 was located in a difference synthesis and refined freely. All non-H atoms were modeled with anisotropic displacement parameters, and the refinement converged to a conventional R1 of 4.33% (based on F and 6047 data with F > 4$\sigma(F)$) with wR2 = 9.26% (based on F^2 and all 7631 data used during refinement) for 501 parameters. The final difference map extrema were +0.49 and −0.39 e Å^3.

Supporting Information Available: X-ray crystallographic files, in CIF format, for compound **2** and thermal ellipsoid plot for [PhP(NH^{i}Pr)$_3$]Br are available through the Internet only. Cyclic voltammogram of compound **2** (1 page). See any current masthead page for ordering and Internet access instructions.

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