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Structural Characterization of Cationic 16-Electron Half-Sandwich Ruthenium Phosphine Complexes with and without Agostic Interaction

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Despite the well-known capabilities of the pentamethylcyclopentadienyl-ruthenium bis(phosphine) auxiliary for binding and activating a wide range of small molecules,[1] cases of genuine coordinatively unsaturated half-sandwich ruthenium phosphine complexes being not stabilized by π-donation from heteroatomic anionic ligands such as halides[2] or alkoxides[3] through metal−ligand multiple bonds are unknown to date. Cationic 16-electron species of the type $[(C_5R_5)RuP_2]^+$ (R = H, Me) have been often postulated as intermediates in most reactions involving 18-electron complexes of the type $[(C_5R_5)RuXP_2]$, but so far they have proven to be elusive to isolation and characterization. A report claimed the synthesis of the supposedly 16-electron complex [CpRu(dcpe)]-$[CF_3SO_3]$ (dcpe = 1,2-bis(dicyclohexyl)phosphinoethane) as an orange solid which was characterized by NMR spectroscopy and microanalysis.[4] However, in view of its color, and the ability of the $[CF_3SO_3]^-$ anion to coordinate at Ru^{II}, this compound is thought to be actually an 18-electron species, namely [CpRu(η^1-(O)-CF_3SO_3)(dcpe)].[5] Very recently, remarkably stable cationic 16-electron complexes of the type $[(C_5R_5)Ru(N\text{-}N)][BAr'_4]$ (R = Me, N-N = TMEDA,[6a] $Me_2NCH_2CH_2N^tBu_2$;[6b] R = H, N-N = TMEDA;[5] Ar′ = 3,5-$C_6H_3(CF_3)_2$) have been described and characterized by X-ray crystallography. Their stability has been attributed to the hard σ-donor character of the TMEDA ligand.[7] Amidinate ligands are also capable of stabilizing coordinatively unsaturated metal centers in neutral complexes of the type [Cp*Ru(amidinate)],[7] due to weak coordination of π-electrons on the amidinate ligand. Similar compounds containing phosphorus donor ligands remain unknown. We have now found that the complex [Cp*RuCl(dippe)] (dippe = 1,2-diisopropylphosphino)ethane)[8] reacts with $NaBAr'_4$ in fluorobenzene under argon, furnishing the cationic 16-electron complex [Cp*Ru(dippe)]-$[BAr'_4]$ (**1**).[9] In analogous fashion, coordinatively unsaturated $[Cp^*Ru(PMe^iPr_2)_2][BAr'_4]$ (**2**)[10] was obtained by treatment of $[Cp^*RuCl(PMe^iPr_2)]$[11] with 1 equiv of PMe^iPr_2 and $NaBAr'_4$ in fluorobenzene under argon. Both compounds are very air-sensitive and are deep blue, a characteristic feature exhibited by other 16-electron half-sandwich ruthenium complexes.[2,3,5,6] A strong band in the UV−vis spectrum (CH_2Cl_2 solution) at 686 nm for **1**, and at 617 nm (with a shoulder at 715 nm) for **2**, is responsible for this blue color. The X-ray crystal structures of **1** and **2** were determined.[12] Both complex cations possess "two-legged" piano stool structures with significant differences in the orientation of the P-bonded alkyl groups relative to the Cp* moieties. Interestingly, $[Cp^*Ru(dippe)]^+$ is stabilized by an agostic interaction with one of the hydrogen atoms of an isopropyl group (Figure 1), whereas such an interaction is absent in the case of $[Cp^*Ru(PMe^iPr_2)_2]^+$ (Figure 2). The observed Ru···C(25) separation is 2.953(4) Å (calculated Ru−H(25a) bond distance, 2.262 Å). The Ru···C(25) distance is only slightly longer than the average Ru···C value of 2.875 Å observed in the complex [RuPh(CO)-

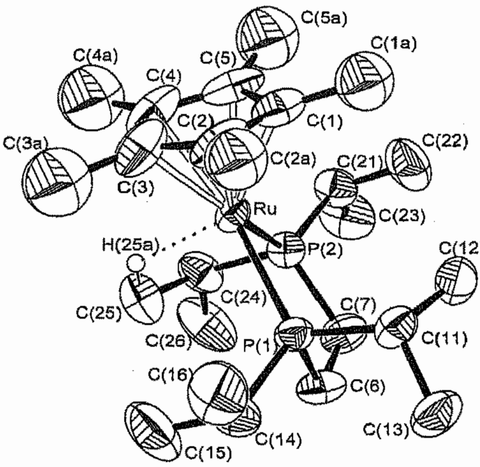

Figure 1. Molecular structure of the cation $[Cp^*Ru(dippe)]^+$ in **1**. Relevant bond lengths (Å) and angles (deg): Ru−C(1), 2.179(3); Ru−C(2), 2.235(3); Ru−C(3), 2.211(3); Ru−C(4), 2.205(3); Ru−C(5), 2.203(3); Ru−P(1), 2.331(1); Ru···C(25), 2.953(4); Ru···H(25a), 2.262 (calculated); Ru−P(2), 2.356(1); P(1)−Ru−P(2), 83.13(4).

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(9) Spectral data for **1**: ^1H NMR (400 MHz, CD_2Cl_2, 193 K) δ −4.94 (1 H, br, Ru-*H*-CH_2), 0.60, 0.84 (m br, $P(CH(CH_3)_2)_2$), 1.43 (s, $C_5(CH_3)_5$), 1.60 (d, PCH_2), 2.43 (m br, $P(CH(CH_3)_2)_2$); $^{31}P\{^1H\}$ NMR (161.89 MHz, CD_2Cl_2, 193 K) δ 81.3; $^{13}C\{^1H\}$ NMR (201.12 MHz, CD_2Cl_2, 193 K) δ 10.8 (s, $C_5(CH_3)_5$), 16.6, 17.2 (s, $P(CH(CH_3)_2)_2$), 18.1 (m, PCH_2), 26.2 (m, $P(CH(CH_3)_2)_2$), 83.2 (s, $C_5(CH_3)_5$).

(10) Spectral data for **2**: ^1H NMR (400 MHz, CD_2Cl_2, 198 K) δ 0.67, 1.10 (m br, $P(CH(CH_3)_2)_2$), 1.34 (s, $C_5(CH_3)_5$), 1.48 (m, PCH_3), 2.13 (m br, $P(CH(CH_3)_2)_2$); $^{31}P\{^1H\}$ NMR (161.89 MHz, CD_2Cl_2, 198 K) δ 26.7; $^{13}C\{^1H\}$ NMR (201.12 MHz, CD_2Cl_2, 198 K) δ 3.27 (m, PCH_3), 11.0 (s, $C_5(CH_3)_5$), 17.6, 19.1 (s, $P(CH(CH_3)_2)_2$), 26.9 (d, J(C, P) = 22 Hz, $P(CH(CH_3)_2)_2$), 79.9 (s, $C_5(CH_3)_5$).

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(12) Crystals of **1** suitable for X-ray structure analysis were obtained by slow diffusion of petroleum ether into a concentrated fluorobenzene solution at room temperature. Crystal dimensions: 0.7 × 0.7 × 0.7 mm, triclinic, space group $P1$, $a = 12.597(6)$, $b = 12.946(6)$, and $c = 18.967(9)$ Å, $\alpha = 95.40(2)$, $\beta = 99.62(2)$, and $\gamma = 92.78(2)°$, $V = 3030(2)$ Å^3, FW = 1361.85, $Z = 2$, $F(000) = 1380$, $\rho_{calcd} = 1.493$ g cm^{-3}, $\mu = 4.21$ cm^{-1}, $T = 213 \pm 2$ K, Siemens SMART CCD diffractometer, Mo Kα radiation ($\lambda = 0.71073$ Å, graphite monochromator); 17 192 unique and 14 100 observed ($I > 2\sigma(I)$, $R_{int} = 0.021$) reflections; $R = 0.054$ (0.066) ($R_w = 0.157$); residual electron density peaks +1.03 and −0.70 e Å^{-3}. Crystals of **2** suitable for X-ray structure analysis were obtained by slow diffusion of petroleum ether into a concentrated fluorobenzene solution at room temperature. Crystal dimensions: 0.7 × 0.7 × 0.8 mm, monoclinic, space group $P2_1$, $a = 12.474(5)$, $b = 18.974(8)$, and $c = 13.003(5)$ Å, $\beta = 92.68(2)°$, $V = 3074(2)$ Å^3, FW = 1363.87, $Z = 2$, $F(000) = 1384$, $\rho_{calcd} = 1.473$ g cm^{-3}, $\mu = 4.15$ cm^{-1}, $T = 223 \pm 2$ K, Siemens SMART CCD diffractometer, Mo Kα radiation ($\lambda = 0.71073$ Å, graphite monochromator); 17 644 unique and 15 719 observed ($I > 2\sigma(I)$, $R_{int} = 0.021$) reflections; $R = 0.061$ (0.068) ($R_w = 0.179$), residual electron density peaks +1.36 and −1.04 e Å^{-3}.

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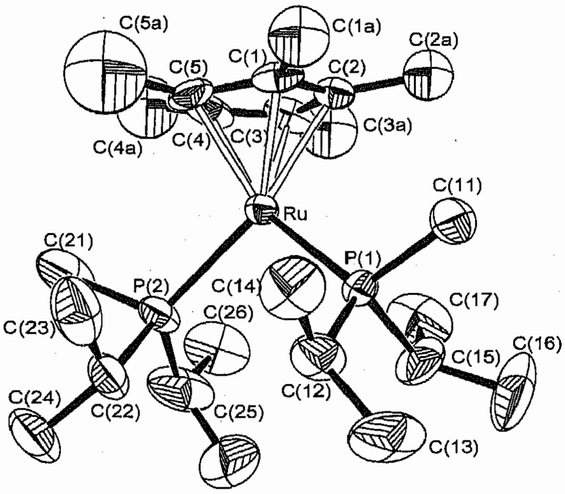

Figure 2. Molecular structure of the cation [Cp*Ru(PMe^{i}Pr$_2$)$_2$]$^+$ in **2**. Relevant bond lengths (Å) and angles (deg): Ru–C(1), 2.198(4); Ru–C(2), 2.205(5); Ru–C(3), 2.175(6); Ru–C(4), 2.206(5); Ru–C(5), 2.126(5); Ru–P(1), 2.3952(12); Ru–P(2), 2.3932(14); P(1)–Ru–P(2), 101.43(5).

(PMe^{t}Bu$_2$)$_2$][BAr'$_4$], which contains two strong agostic interactions with C–H groups from ^{t}Bu groups on different phosphines.[13] The angle Ru–P(2)–C(24) has a value of 99.45°, whereas for nonagostic isopropyl groups the angles lie in range 117–124°. As a consequence of the agostic interaction, the {[Cp*RuP$_2$]$^+$} moiety adopts a bent conformation, in which the angle formed by the plane containing the atoms P(1)–Ru–P(2) and the plane defined by the C$_5$ ring of the Cp* ligand is 69.4(1)°. In contrast to this, the degree of pyramidalization for [Cp*Ru(PMe^{i}Pr$_2$)$_2$]$^+$ is minimal, as inferred from the value of 80.7(2)° found for the same angle in the case of **2**, not far from perpendicularity. Hence, the cation [Cp*Ru(PMe^{i}Pr$_2$)$_2$]$^+$ has actually a pseudo-C_{2v} structure, similar to that observed for the compounds [Cp*RuX(PR$_3$)],[2,3] [Cp*Ru(TMEDA)][BAr'$_4$],[5] and [Cp*Ru(amidinate)].[7] The [BAr'$_4$]$^-$ anions are separated from the complex cations by van der Waals contacts and do not interact with the metal centers. The ^{1}H NMR spectrum of **1** in CD$_2$Cl$_2$ at 193 K displays one broad resonance at −4.94 ppm attributable to the agostic proton. The ^{31}P{^{1}H} NMR spectrum consists of one singlet at this temperature, and no decoalescence has been observed. This suggests that there is a rapid hydrogen scrambling with all of the isopropyl protons of the dippe ligand, rendering the phosphorus atoms equivalent in the NMR time scale. The NMR spectra of **2** are very simple, as expected for a compound having C_{2v} symmetry, and no signs of agostic interactions are detected. These data clearly indicate that the coordinatively unsaturated character of **1** is partially compensated by an agostic interaction occurring both in the solid state and in solution. On the other hand, **2** is a genuine 16-electron species that shows no stabilization by agostic interaction. The shortest contact between Ru and any of the isopropyl carbon atoms is Ru···C(17), 3.303(13) Å (shortest calculated R–H distance, 2.67 Å to H(17a)), too far for agostic donation. Furthermore, it is interesting to notice that in [Cp*Ru(PMe^{i}Pr$_2$)$_2$]$^+$ the isopropyl groups are all directed away from the region perpendicular to the RuP$_2$ plane, supporting the conclusion that this complex cation does not need to be stabilized by agostic donation. The main chemical difference between **1** and **2** is just the use of either one bidentate phosphine or two monodentate phosphines as coligands, although both of them have similar steric and electron-releasing properties. The chelating nature of the dippe ligand imposes a P(1)–Ru–P(2) bite angle of 83.13(4)° in **1**, considerably smaller than the P(1)–Ru–P(2) angle of 101.43(5)° found for **2**. It seems that the smaller angle P(1)–Ru–P(2) imposed by the chelating phosphine in the case of **1** lowers the energy of the LUMO, in such a way that agostic donation becomes feasible. This appears to be in connection to the observed degree of pyramidalization. According to initial MO calculations made on the isoelectronic d^6 fragment [CpMn(CO)$_2$], a bent structure with C_s symmetry is preferred in the ground state for 16-electron half-sandwich complexes.[14] However, more recent theoretical investigations have shown that pure σ-donor ligands, e.g., H$^-$, favor the existence of an orthogonal structure with C_{2v} symmetry.[3,15] Further studies have shown that whether the structure is orthogonal or bent may depend on whether the complex adopts $S = 0$ or $S = 1$ spin configurations.[16] According to these studies, an increase of electron density in the LUMO in these systems, e.g., when passing from a 16- to an 18-electron configuration, causes an increase in pyramidalization, just as we have observed for **1**. On the other hand, the agostic interaction should not change significantly the electron density at the metal, so caution must be taken in order to avoid a overinterpretation of these results. We are interested in the electronic structure of complexes **1** and **2**, and our structural data will be used for performing calculations on these novel systems based on experimental grounds. Whereas the chemistry of the [Cp*Ru(dippe)]$^+$ moiety has been thoroughly explored,[8,17] we have just started to look at the reactivity of complex **2**, which apparently parallels that of its dippe counterpart, in particular the ability to undergo oxidative addition reactions with hydrogen to yield the dihydride [Cp*RuH$_2$(PMe^{i}Pr$_2$)$_2$]$^+$,[11] and with 1-alkynes furnishing Ru^{IV} hydrido-alkynyl derivatives of the type [Cp*RuH(C≡CR)(PMe^{i}Pr$_2$)$_2$]$^+$.

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Supporting Information Available: Listing of crystallographic information file (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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