

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

Manuel Jiménez Tenorio,[§] Kurt Mereiter,[‡]
M. Carmen Puerta,^{*,§} and Pedro Valerga[§]

Departamento de Ciencia de Materiales e Ingeniería
Metalúrgica y Química Inorgánica, Facultad de Ciencias
Universidad de Cádiz, Apartado 40,
11510 Puerto Real, Cádiz, Spain
Institute of Mineralogy, Crystallography, and Structural
Chemistry, Vienna University of Technology
Getreidemarkt 9, A-1060 Vienna, Austria

Received June 1, 2000

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 halides² or alkoxides³ 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 $[CpRu(dcppe)]-[CF_3SO_3]$ ($dcppe = 1,2$ -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 $[CpRu(\eta^1-O)CF_3SO_3(dcppe)]$.⁵ Very recently, remarkably stable cationic 16-electron complexes of the type $[(C_5R_5)Ru(N-N)][BAR'_4]$ ($R = Me, N-N = TMEDA$,^{6a} $Me_2NCH_2CH_2N^iBu_2$,^{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)ethane⁸ 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

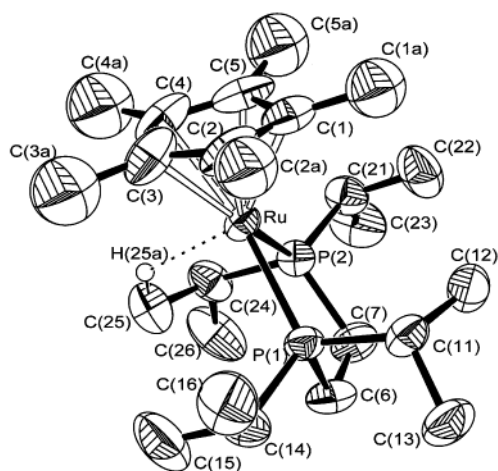


Figure 1. Molecular structure of the cation $[Cp^*Ru(dippe)]^+$ in **1**. Relevant bond lengths (Å) and angles (deg): Ru–C(1), 2.179(3); Ru–C(2), 2.235(3); Ru–C(3), 2.211(3); Ru–C(4), 2.205(3); Ru–C(5), 2.203(3); Ru–P(1), 2.331(1); Ru···C(25), 2.953(4); Ru···H(25a), 2.262 (calculated); Ru–P(2), 2.356(1);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

$[Cp^*RuCl(PMe^iPr_2)_2]$ 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 $Ru\cdots C(25)$ separation is 2.953(4) Å (calculated $Ru-H(25a)$ bond distance, 2.262 Å). The $Ru\cdots C(25)$ distance is only slightly longer than the average $Ru\cdots C$ value of 2.875 Å observed in the complex $[RuPh(CO)-$

(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, $C_5(CH_3)_5$).

(11) Jiménez Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Organomet. Chem.* **2000**, *609*, 161.

(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: $0.7 \times 0.7 \times 0.7$ 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 $\gamma = 92.78(2)^\circ$, $V = 3030(2)$ Å³, $FW = 1361.85$, $Z = 2$, $F(000) = 1380$, $\rho_{calcd} = 1.493$ g cm^{–3}, $\mu = 4.21$ cm^{–1}, $T = 213 \pm 2$ K, Siemens SMART CCD diffractometer, Mo $K\alpha$ 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: $0.7 \times 0.7 \times 0.8$ mm, monoclinic, space group $P2_1$, $a = 12.474(5)$, $b = 18.974(8)$, and $c = 13.003(5)$ Å, $\beta = 92.68(2)^\circ$, $V = 3074(2)$ Å³, $FW = 1363.87$, $Z = 2$, $F(000) = 1384$, $\rho_{calcd} = 1.473$ g cm^{–3}, $\mu = 4.15$ cm^{–1}, $T = 223 \pm 2$ K, Siemens SMART CCD diffractometer, Mo $K\alpha$ 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}.

[§] Universidad de Cádiz.

[‡] Vienna University of Technology.

(1) Davies, S. G.; McNally, A. J.; Smallridge, A. J. *Adv. Organomet. Chem.* **1990**, *30*, 1.

(2) (a) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Chem. Soc., Chem. Commun.* **1988**, 278. (b) Arliguie, T.; Border, C.; Chaudret, B.; Devillers, J.; Poilblanc, R. *Organometallics* **1989**, *8*, 1308.

(3) Johnson, T. J.; Foltig, K.; Streib, W. E.; Martin, J. D.; Huffman, J. C.; Jackson, S. A.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1995**, *34*, 488.

(4) Joslin, F. L.; Johnson, M. P.; Mague, J. T.; Roundhill, D. M. *Organometallics* **1991**, *10*, 2781.

(5) Gemel, C.; Huffman, J. C.; Caulton, K. G.; Mauthner, K.; Kirchner, K. *J. Organomet. Chem.* **2000**, *593–594*, 342.

(6) (a) Gemel, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1997**, *16*, 5601. (b) Gemel, C.; Sapunov, V. N.; Mereiter, K.; Ferencic, M.; Schmid, R.; Kirchner, K. *Inorg. Chim. Acta* **1999**, *286*, 114.

(7) Yamaguchi, Y.; Nagashima, H. *Organometallics* **2000**, *19*, 725.

(8) de los Ríos, I.; Jiménez Tenorio, M.; Padilla, J.; Puerta, M. C.; Valerga, P. *J. Chem. Soc., Dalton Trans.* **1996**, 377.

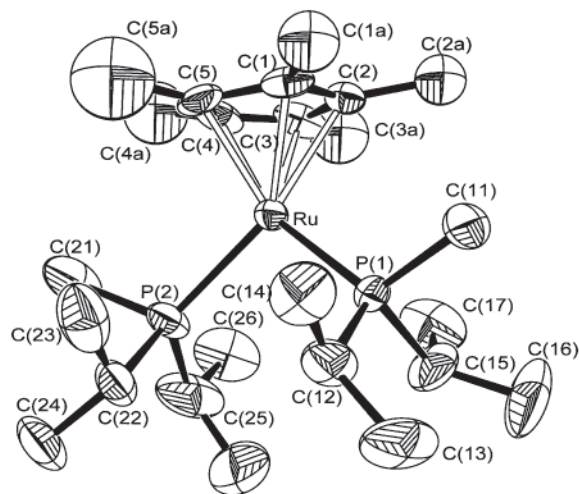


Figure 2. Molecular structure of the cation $[\text{Cp}^*\text{Ru}(\text{PMe}^i\text{Pr}_2)_2]^+$ in **2**. Relevant bond lengths (Å) and angles (deg): Ru–C(1), 2.198(4); Ru–C(2), 2.205(5); Ru–C(3), 2.175(6); Ru–C(4), 2.206(5); Ru–C(5), 2.126(5); Ru–P(1), 2.3952(12); Ru–P(2), 2.3932(14); P(1)–Ru–P(2),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

$(\text{PMe}^i\text{Bu}_2)_2][\text{BAR}'_4]$, which contains two strong agostic interactions with C–H groups from ^iBu 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 $\{[\text{Cp}^*\text{RuP}_2]^+\}$ 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 $[\text{Cp}^*\text{Ru}(\text{PMe}^i\text{Pr}_2)_2]^+$ 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 $[\text{Cp}^*\text{Ru}(\text{PMe}^i\text{Pr}_2)_2]^+$ has actually a pseudo- C_{2v} structure, similar to that observed for the compounds $[\text{Cp}^*\text{RuX}(\text{PR}_3)_2]$,^{2,3} $[\text{Cp}^*\text{Ru}(\text{TMEDA})][\text{BAR}'_4]$,⁵ and $[\text{Cp}^*\text{Ru}(\text{amidinate})]$.⁷ The $[\text{BAR}'_4]^-$ anions are separated from the complex cations by van der Waals contacts and do not interact with the metal centers. The ^1H NMR spectrum of **1** in CD_2Cl_2 at 193 K displays one broad resonance at –4.94 ppm attributable to the agostic proton. The $^{31}\text{P}\{^1\text{H}\}$ 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

(13) (a) Huang, D.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2004. (b) Huang, D.; Streib, W. E.; Bollinger, J. C.; Caulton, K. G.; Winter, R. F.; Scheiring, T. *J. Am. Chem. Soc.* **1999**, *121*, 8087.

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 $[\text{Cp}^*\text{Ru}(\text{PMe}^i\text{Pr}_2)_2]^+$ 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 $[\text{Cp}^*\text{Mn}(\text{CO})_2]$, 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 an 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 $[\text{Cp}^*\text{Ru}(\text{dippe})]^+$ 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 $[\text{Cp}^*\text{RuH}_2(\text{PMe}^i\text{Pr}_2)_2]^+$,¹¹ and with 1-alkynes furnishing Ru^{IV} hydrido-alkynyl derivatives of the type $[\text{Cp}^*\text{RuH}(\text{C}\equiv\text{CR})(\text{PMe}^i\text{Pr}_2)_2]^+$.

Acknowledgment. We thank the Ministerio de Educación y Cultura of Spain (DGICYT, Project PB97-1357, Accion Integrada HU-1998-0026) for financial support, Johnson Matthey plc for generous loans of ruthenium trichloride, and the Royal Society of Chemistry for the award of a grant for international authors (to M.J.T.).

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

JA001928U

(14) Hofmann, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 536.

(15) Ward, T. R.; Schafer, O.; Daul, C.; Hofmann, P. *Organometallics* **1997**, *16*, 3207.

(16) Costuas, K.; Saillard, J. Y. *Organometallics* **1999**, *18*, 2505.

(17) (a) de los Ríos, I.; Jiménez Tenorio, M.; Padilla, J.; Puerta, M. C.; Valerga, P. *Organometallics* **1996**, *15*, 4565. (b) de los Ríos, I.; Jiménez Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Am. Chem. Soc.* **1997**, *119*, 652.