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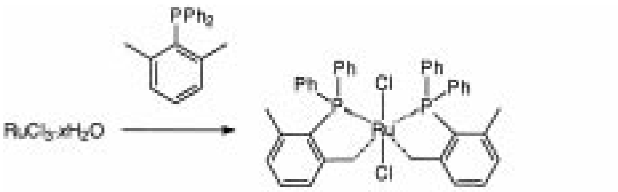
[14] Strictly speaking, this calculation is only valid for fast exchange (ca. 1 ms) between the bound and the free surfactant fraction on the timescale of the correlation function. For slow exchange, the autocorrelation function [Eq. (1)] will consist of two components with different diffusion coefficients. No significant deviation from Equation (1) was observed in our experiments, however.

$[RuCl_2\{PPh_2(2,6\text{-}Me_2C_6H_3)\}_2]$: A Neutral 14-Electron Ruthenium(II) Complex with Two Agostic Interactions**

Walter Baratta,* Eberhardt Herdtweck, and Pierluigi Rigo

Coordinatively unsaturated transition metal complexes, which play a key role in many catalytic processes, have been often obtained with bulky tertiary phosphanes (PR_3) as ligands that provide steric protection to the empty coordination sites at the metal. The steric crowding forces the R group of the ligand in close proximity to the metal center to induce an agostic interaction[1] between a C–H bond in the R group and the metal atom, thus preventing dimerization or solvent coordination. Ruthenium(II) complexes with small phosphanes are generally six-coordinate 18-electron species of the type $[RuX_2(PR_3)_4]$ (X = halide), whereas with the bulky triarylphosphanes five-coordinate 16-electron complexes such as $[RuCl_2(PPh_3)_3]$ are formed.[2] La Placa and Ibers noted that the close approach of one *ortho*-phenyl hydrogen atom to the metal effectively blocks a coordination site at the ruthenium center.[3] It can be anticipated that when the *ortho*-hydrogen atom of the phenyl rings of PPh_3 are substituted with methyl groups, stronger contacts would occur; the CH_3 group is forced close to metal center, and an agostic interaction is favored. With this in mind, we have been investigating ruthenium(II) complexes with *ortho*-methyl-substituted arylphosphane ligands.

We report herein the isolation and characterization in solution and in the solid state of the formally four-coordinate complex $[RuCl_2\{PPh_2(2,6\text{-}Me_2C_6H_3)\}_2]$ (**1**), in which the two empty coordination sites on the metal are occupied by one of the methyl groups of each xylyl substituent. No neutral monomeric bis-phosphane 14-electron species have been reported until now, the complexes of stoichiometry $[RuCl_2(PR_3)_2]$ (R = Ph, $3\text{-}C_6H_4SO_3H$)[4, 5] being binuclear derivatives with Ru(μ-Cl)Ru bridges. Recently, the dihydrogen complexes $[RuXX'(H_2)L_2]$ (X, X' = halogen, H; L = P*i*Pr$_3$, P*t*Bu$_2$Me) have been used as suitable sources of 14-electron complexes $[RuXX'L_2]$ for the preparation of ruthenium(II) carbene and vinylidene derivatives.[6] Complex **1** is the first example of a neutral ruthenium complex with two agostic interactions, and it can be compared with the recently reported cationic complex [Ru(Ph)(CO)(P*t*Bu$_2$Me)$_2$]$^+$[BAr'$_4$]$^-$ (Ar' = 3,5-$(CF_3)_2C_6H_3$).[7]



(a)

Reaction of ruthenium trichloride hydrate with a threefold molar amount of (2,6-dimethylphenyl)diphenylphosphane in refluxing methanol afforded the purple, diamagnetic ruthenium complex **1** in good yield [Eq. (a)]. Compound **1** is thermally stable in solution for many hours at room temperature if no air is admitted. The $^{31}P\{^1H\}$ NMR spectra of **1** in different solvents and at different temperatures show only one sharp signal. Therefore, solvent coordination to the ruthenium center or formation of dimeric complexes of the type $[Ru_2Cl_2(\mu\text{-}Cl)_2(PR_3)_4]$ (R = Ph, $3\text{-}C_6H_4SO_3H$),[4, 5] having two nonequivalent phosphane ligands, can be excluded. Moreover, the temperature dependence of the ^1H NMR spectra shows the fluxional behavior of **1** in solution. In fact, above 50 °C the resonances of the methyl protons appear as a broad signal ($\delta = 1.92$ in $C_2Cl_4D_2$ at 80 °C). Upon lowering of the temperature the signal splits into two broad resonances of equal intensity ($\delta = 2.37$ and 1.37 in $C_2Cl_4D_2$ at 20 °C), indicating that the xylyl rotation is slow on the ^1H NMR time scale. Furthermore, below -40 °C the resonance at $\delta = 1.37$ becomes sharp, while that at $\delta = 2.37$ splits into a doublet (J(H,P) = 5.1 Hz). Consequently the low-field signal can be attributed to the protons of the methyl group close to the ruthenium atom that couple with one phosphane phosphorus atom. No further splitting of this signal was observed even at -90 °C, so rotation of the interacting CH_3 group cannot be frozen out. The $^{13}C\{^1H\}$ NMR spectrum of **1** in $CDCl_3$ at 20 °C shows two nonbinomial quintets for the *ipso*-carbon atoms of the xylyl and the phenyl groups at $\delta = 134.5$ and $\delta = 132.0$, respectively, which are in agreement with a *cis* arrangement of the two phosphane ligands.[8] At room temperature the spectrum of **1** exhibits two broad signals for the methyl carbon atoms at $\delta = 23.7$ and 11.7. Whereas the first resonance becomes sharp below -20 °C, and is therefore assigned to the noninteracting methyl groups (CH_3 of the free phosphane:

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$\delta = 23.8$), the second absorption, which is attributed to the interacting methyl group, splits into a triplet with a $|J_{\text{trans}}(\text{C,P})+J_{\text{cis}}(\text{C,P})|$ value of 23.6 Hz due to $^{2}J(\text{P,P})$ virtual coupling (CD_2Cl_2 at $-40\,^{\circ}\text{C}$).[9] These data can be compared with those of a methyl group bound through a δ-agostic interaction in an azine phosphane ruthenium(II) complex ($J(\text{C,P}) = 13.6$ Hz).[10] Furthermore, a ^{13}C NMR INEPT experiment carried out on **1** exhibits a broad quartet at $\delta = 10.5$ with a $^{1}J(\text{C,H})$ value of about 117 Hz, a significantly low value[1a] compared to the $^{1}J(\text{C,H})$ value of 127 Hz shown by the other sharp quartet at $\delta = 23.8$ ($CDCl_3$ at $-40\,^{\circ}\text{C}$). Consequently, all these findings are in agreement with the presence of two strong Ru ··· H–C interactions in the stereochemically rigid complex **1**.

To establish the previous formulation with two methyl groups close to the metal center,[11] an X-ray diffraction study was carried out on a single crystal of the solvate **1** · toluene (Figure 1 a).[12] In the discrete monomeric units of **1** the ruthenium center is in a nearly octahedral environment with two *trans* chloride atoms and two *cis* phosphane ligands. The coordination sphere of ruthenium is completed by two methyl groups of the two xylyl substituents. Complex **1** is nearly C_2-symmetric, with the twofold axis bisecting the P1-Ru-P2 angle. The Ru–Cl and the Ru–P bond lengths are in agreement with those reported for phosphaneruthenium(II) chloride complexes.[13] The chloro atoms are significantly bent away from the phosphorus atoms, presumably to minimize steric interactions with the phenyl groups, resulting in a Cl1-Ru-Cl2 bond angle of 168.00(2)°. The Ru-P-C_{ipso} angles for the xylyl groups of **1** are on average 109.37(5)°, which is about 7.44° smaller than the Ru-P-C_{ipso} angles of the phenyl groups (mean value 116.81(4)°). The five atoms Ru, P1, P2, C10, and C40 are almost coplanar (distances to the mean plane less than ±8 pm) and the atom pairs C11/C12 and C41/C46 are in C_2-symmetrical positions with respect to this plane (+44/+53 and −50/−50 pm, respectively). Owing to the steric crowding the xylyl groups are all bent back, and hinged about the P1–C10 and P2–C40 axes at an angle of 20.3° and 20.6°, respectively; one phenyl ring lies above and the other below the principal coordination plane (Figure 1 b).

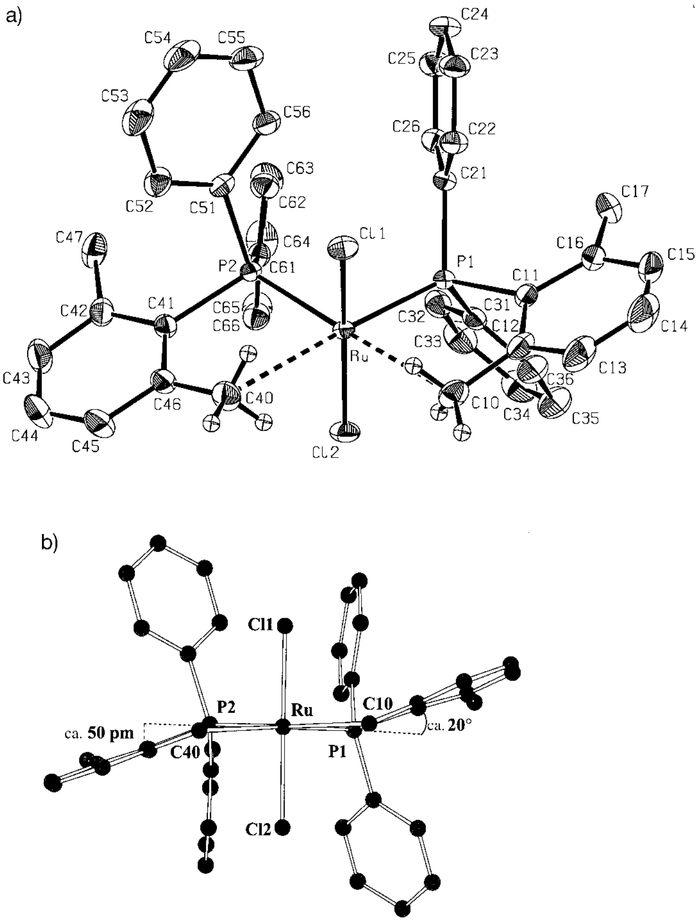

Figure 1. a) ORTEP drawing of the structure of **1**. Thermal ellipsoids are at the 50% probability level. Selected bond lengths [pm] and angles [°]: Ru–Cl1 239.94(4), Ru–Cl2 239.76(4), Ru–P1 225.82(4), Ru–P2 225.25(3), Ru ··· C10 265.3(2), Ru ··· C40 264.9(2); Cl1-Ru-Cl2 168.00(2), Cl1-Ru-P1 94.69(2), Cl1-Ru-P2 92.93(2), Cl2-Ru-P1 92.42(2), Cl2-Ru-P2 95.05(2), P1-Ru-P2 101.91(1), C10 ··· Ru ··· C40 102.18(5), P1-Ru ··· C10 78.17(4), P2-Ru ··· C40 77.94(4); b) Perspective view of **1** approximately parallel to the mean plane made up of Ru, P1, P2, C10, and C40.

The X-ray analysis clearly confirms that complex **1** shows two agostic Ru ··· H–C interactions, through the coordination of one methyl group of each phosphane ligand. The shortest Ru ··· C(10/40) distances are on average 265.1(2) pm, a value which is within the range of very strong agostic interactions. In fact, in the cationic complex $[\text{Ru(Ph)(CO)}(\text{P}t\text{Bu}_2\text{Me})_2]^+[\text{BAr}'_4]^-$ the distances of the two methyl groups involved in an agostic interaction are 287 and 288 ppm,[7] while the reported Ru–C bond lengths for alkyl- and arylruthenium(II) derivatives are in the range of 204–222 pm.[14]

Apparently, in **1** the phosphane $PPh_2(2,6\text{-}Me_2C_6H_3)$ behaves as a "bidentate" ligand to give a five-membered ring in which a methyl group acts as two-electron donor, yielding a formally pentacoordinate methyl carbon atom.[15] However, only a neutron diffraction experiment of **1** will provide clear-cut evidence of the coordination mode of the bridging methyl groups. With the related mono-*ortho*-methylated phosphanes $PPh_n(2\text{-}MeC_6H_4)_{3-n}$ ($n = 0-2$), we were unable to obtain complexes of the type $[RuCl_2(PR_3)_2]$. Moreover, **1** presents strong similarities to the dihalogenruthenium(II) complexes with unsymmetrical bidentate ligands containing phosphorus and a second weaker donor functionality such as oxygen. In particular, the ligands PPh_2Ar (Ar = 2-$MeOC_6H_4$, 2,6-$(MeO)_2C_6H_3$) form the six-coordinate complexes $[RuCl_2(PPh_2Ar)_2]$,[16] which have geometrical features similar to **1**.

Complex **1**, which is accessible on a gram scale, appears to be attractive for manifold catalytic applications owing to the availability of two free coordination sites for substrate binding. Accordingly, **1** promptly reacts with carbon monoxide at ambient conditions to yield carbonylruthenium derivatives. We are currently investigating the extension of the coordination chemistry of the "chelating" phosphane $PPh_2(2,6\text{-}Me_2C_6H_3)$ to the neighboring elements.

Experimental Section

All operations were carried out with dry solvents and under an argon atmosphere. The NMR spectra were recorded on a Brucker AC200 spectrometer.

1: $RuCl_3 \cdot xH_2O$ (Aldrich) (0.300 g, 1.2 mmol) was dissolved in methanol (10 mL) by bringing the mixture to a boil. $PPh_2(2,6\text{-}Me_2C_6H_3)$ (1.00 g, 3.44 mmol) was added, and the solution was refluxed for 1 h to afford a purple precipitate. After filtration the product was washed with diethyl ether and dried under reduced pressure. Yield: 0.550 g (60%). ^1H NMR (200.1 MHz, CD_2Cl_2, $-50\,^\circ C$, TMS): $\delta = 7.45-6.75$ (m, 26H; aromatic protons), 2.37 (d, $J(H,P) = 5.1$ Hz, 6H; CH_3), 1.30 (s, 6H; CH_3); $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, $-50\,^\circ C$, TMS): $\delta = 142.6$ (s; *C*Me), 142.1 (pseudo t, $J(C,P) = 8.8$ Hz; *C*Me), 133.7 (nonbinomial quint., *ipso*-C_6H_3), 132.8 (pseudo t, $J(C,P) = 4.3$ Hz; *o*-C_6H_5), 131.4 (nonbinomial quint., *ipso*-C_6H_5), 131.0 (s; *p*-C_6H_3), 130.2 (brs; *m*-C_6H_3), 129.7 (s; *p*-C_6H_5), 128.6 (pseudo t, $J(C,P) = 5.3$ Hz; *m*-C_6H_3), 127.9 (pseudo t, $J(C,P) = 5.1$ Hz; *m*-C_6H_5), 23.7 (s; CH_3), 10.1 (pseudo t, $J(C,P) = 11.8$ Hz; CH_3); $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, $-50\,^\circ C$, H_3PO_4): $\delta = 56.2$; elemental analysis calcd for $C_{40}H_{38}Cl_2P_2Ru$: C 63.8, H 5.1; found: C 63.1, H 5.0.

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[11] Although the IR spectrum (KBr) of **1** shows weak absorption bands at 2736, 2676, 2615, and 2574 cm^{-1}, which are in the range of agostic C–H stretching frequencies,[1a] these are more likely combination bands.

[12] Crystal structure analysis of **1** · toluene: $C_{40}H_{38}Cl_2P_2Ru \cdot C_7H_8$: $M_r = 844.80$, triclinic, space group $P\bar{1}$, $a = 1060.63(7)$, $b = 1279.63(10)$, $c = 1498.12(10)$ pm, $\alpha = 90.202(8)$, $\beta = 89.943(8)$, $\gamma = 96.509(9)^\circ$, $V = 2020.2(2) \times 10^6$ pm^3; $Z = 2$; $\rho_{calcd} = 1.389$ g cm^{-3}, $F_{000} = 872$, $\mu = 6.3$ cm^{-1}. Suitable crystals were obtained by cooling a concentrated solution of **1** in toluene. Preliminary examination and data collection were carried out on a STOE Imaging Plate Diffraction System equipped with a rotating anode (NONIUS FR591) and graphite-monochromated $Mo_{K\alpha}$ radiation. Data were collected at 193 K within the Θ range $2.65^\circ < \Theta < 27.75^\circ$. A total of 33597 reflections were collected. After merging ($R_{int} = 0.0263$), 8706 independent reflections remained and were used to refine 653 parameters. Data were corrected for Lorentz and polarization effects. The structure was solved by a combination of direct methods and difference-Fourier syntheses. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located by difference Fourier synthesis and refined with individual isotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ (*SHELXL-93*) and converged (all data) with $R1 = 0.0235$, $wR2 = 0.0569$, GOF = 1.063, and shift/error < 0.002. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for X-Ray Crystallography*.[17] All calculations were performed on a DEC 3000 AXP workstation with the *STRUX-V*[18] system, including the programs *PLATON-92*, *PLUTON-92*,[19] *SIR-92*,[20] and *SHELXL-93*.[21] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-111368. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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