Solution and Solid-State Structure of Ru(CO)₂(Bu₂P^tC₂H₄P^tBu₂): Square Planar and Monomeric?

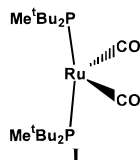Torsten Gottschalk-Gaudig, John C. Huffman, and
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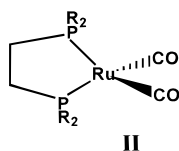Université de Montpellier 2
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We seek to add a new dimension to the chemistry of isolable, zerovalent unsaturated Ru(CO)₂(P^tBu₂Me)₂, **I**,[1a] which is super-

I

ficially analogous to the transients Ru(CO)₄,[1b] Ru(CO)₂(PMe₃)₂ [2] and Ru(Me₂PC₂H₄PMe₂)₂.[3] In particular, we wished to "tie together" the two methyl groups in Ru(CO)₂(P^tBu₂Me)₂ to establish the consequences of imposing a *cis*-P₂ stereochemistry; presumably, this must make a less stable (hence more reactive) isomeric form since monodentate phosphines reveal the preferred structure **I** when chelate constraints are absent. Matrix isolation of Ru(CO)₂(Me₂PC₂H₄PMe₂) has been accomplished,[4] and comparison of species in solution to matrix isolation could reveal the sensitivity of such species to external influence and substituent effects. The desired Ru(CO)₂L₂ (L₂ = ^tBu₂PCH₂CH₂P^tBu₂) was synthesized according to Scheme 1, whose last step abstracts two H ligands using ethylene. The resulting five-coordinate complex Ru(CO)₂(C₂H₄)L₂ loses ethylene simply upon vacuum removal of the volatiles from a benzene solution at 25 °C.

Dark green Ru(CO)₂L₂ possesses some remarkable properties. In benzene or toluene, it shows a single chemical shift at 25 °C for ^tBu protons, for CH₂ protons, for ³¹P and for the carbonyl carbons, and also by ¹H and ³¹P{¹H} NMR at −80 °C. The 25 °C ¹³C{¹H} NMR spectrum of the carbonyl carbons is a doublet of doublets (J_{C-P} = 72 and 18 Hz), inconsistent with a C_{2v} structure ("tetrahedral"), **II**.

II

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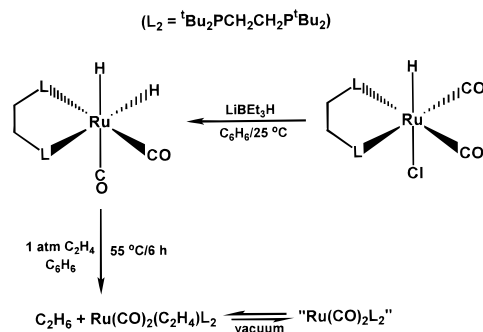‡ E-mail: odile.eisenstein@lsd.univ-montp2.fr.
(1) (a) Ogasawara, M.; Macgregor, S. A.; Streib, W. E.; Folting, K.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1995**, *117*, 8869. (b) Bogdan, P. L.; Weitz, E. *J. Am. Chem. Soc.* **1989**, *111*, 3163.
(2) Mawby, R. J.; Perutz, R. N.; Whittlesey, M. K. *Organometallics* **1995**, *14*, 3268.
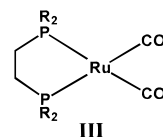(3) Hall, C.; Jones, W. D.; Mawby, R. J.; Osman, R.; Perutz, R. N.; Whittlesey, M. K. *J. Am. Chem. Soc.* **1992**, *114*, 7425.
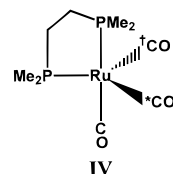(4) Whittlesey, M. K.; Perutz, R. N.; Virrels, I. G.; George, M. W. *Organometallics* **1997**, *16*, 268.

Scheme 1

The observation of two distinct $^2J_{P-CO}$ values indicates that the two phosphorus nuclei are not magnetically equivalent; the impulsive conclusion is that the molecule is rigorously planar **III**,

III

which is surprising compared to the nonplanar geometry deduced for transient Ru(CO)₂(Me₂PC₂H₄PMe₂) in Ar, Xe, and CH₄ matrixes.[4] That structure was based on (1) ν_{CO} infrared intensities in these matrixes and also in heptane and on (2) the large dependence of the electronic spectrum on matrix identity (interaction with Xe and with CH₄ was proposed) and on (3) consideration of the structure of the precursor **IV**.

IV

Geometry optimization of Ru(CO)₂(H₂PC₂H₄PH₂) by DFT-(B3PW91) calculations[5] with no symmetry constraint gives a geometry with two inequivalent CO ligands (Figure 1). The energy required to equivalence the two CO ligands has been calculated on the simpler model *cis*-Ru(CO)₂(PH₃)₂, whose optimized (nonplanar) geometry is found to be very close (P−Ru−C = 151.7 and 168.3°, C−Ru−C = 90.3°, CO = 1.159 Å) to that with the bidentate phosphine ligand, showing that the nonplanar Ru is not associated with the presence of a nonplanar Ru−P−C−C−P ring. The nonplanar transition states for CO exchange have been located, all at energy less than 0.3 kcal.mol⁻¹ above the minimum. The planar C_{2v} structure (0.7 kcal/mol⁻¹ above the minimum) has been shown[6] not to be a transition state for a CO exchange. The extremely small difference in energy between these stationary points is beyond the reliability of the present level of calculation. However, the flatness of the surface (<1 kcal.mol⁻¹) for a large range of P−Ru−C angles (180−150°) is a property of this system (i.e., also obtained with test MP2 calculations). This suggests that all of the structures obtained by varying the two P−Ru−C angles within the 180−150° range are thermally accessible and are also true of the experimental complex with its ^tBu groups. This is in

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(5) All calculations were carried out with the Gaussian 94 package of programs[7] at the DFT(B3PW91) level.[9] Effective core potentials were used for replacing the 28 innermost electrons of Ru[10] and the 10 innermost electrons of P.[11] A basis set was of valence double ζ quality[10−12] with polarization functions on all atoms[13,14] was used.
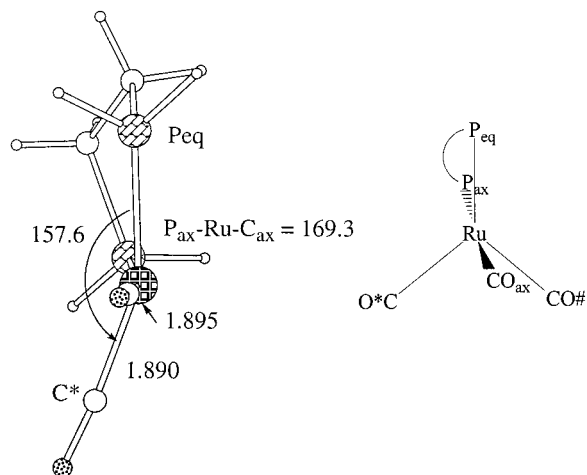(6) Murrell, J. N.; Laidler, K. J. *Trans. Faraday Soc.* **1968**, *64*, 371.

Figure 1. DFT(B3PW91) optimized structure of $Ru(CO)_2(H_2PC_2H_4PH_2)$ (distances in Å, angles in degrees) (left), in relation to the pentacoordinated $Ru(CO)_3(P-P)$ structure upon loss of $CO^\#$ (right).

Figure 2. ORTEP drawing (30% probability ellipsoids) of the nonhydrogen atoms of $[Ru(CO)_2(^tBu_2PC_2H_4P^tBu_2)]_2$ with selected atom labeling. Bond distances (in Å) Ru–Ru = 2.703(1), Ru–P2 = 2.459(2); Ru–P5 = 2.462(2); Ru–C22 = 2.016(7); Ru–C22′ = 2.050(6); C22–O23 = 1.198(7); C24–O25 = 1.165(8).

full agreement with the NMR results which show only one carbonyl carbon and one ^{31}P NMR environment even at low temperature. The geometry and the high fluxionality of the Ru-$(CO)_2(R_2PC_2H_4PR_2)$ complex contrasts significantly with the more strongly nonplanar and less fluxional $Ru(CO)_2(P^tBu_2Me)_2$.[1a] This result is consistent with the fact[4] that $Ru(CO)_2(Me_2PC_2H_4PMe_2)$ is nonplanar, which makes the spectra of this four-coordinate species sensitive to its environment (i.e., solvent or matrix).

The $\angle OC-Ru-CO$ in the optimized DFT structure of Ru-$(CO)_2(H_2PC_2H_4PH_2)$ is 91.6°. The infrared spectrum of $[Ru(CO)_2(^tBu_2PC_2H_4P^tBu_2)]$ in pentane shows bands at 1955 and 1889 cm^{-1}, whose intensities I (1889)/I (1955) = 0.81 give an $\angle OC-Ru-CO$ of 83°. This compares to the C–Ru–C angle of 84° calculated by the same IR intensity method[8] for $Ru(CO)_2(Me_2PC_2H_4PMe_2)$).

The X-ray diffraction study of the green solid reveals that the situation is even more complicated. The structure of green crystals grown from a green 1:8 benzene/pentane solution is shown in Figure 2. The centrosymmetric *dimer* has two bridging carbonyls and a Ru/Ru distance of 2.70 Å. We confirm the complete conversion of solution monomer to solid-state dimer by the infrared spectrum in Nujol: ν_{CO} = 1869 and 1668 cm^{-1}. The cis stereochemistry of the bulky phosphines in the chelate thus permits the aggregation which does not take place for *trans*-$Ru(CO)_2(P^tBu_2Me)_2$, but this does not aggregate to a trimer as seen for $[Ru(CO)_4]_3$. The lack of visible color change between solid and solution is particularly deceptive in this compound, but the solid-state electronic spectrum lacks the band at 424 nm that is seen for the monomer in solution; they both have a band at ~670 nm, however, which is the source of the green color. The observed complete aggregation change of $Ru(CO)_2L_2$ on change of phase is rare behavior for any d^8 species.[15–18] The "softness" to bending CO out of the plane apparently makes addition of a second monomer (i.e., dimerization) possible here at unusually small cost of "deformation energy". This observation and the matrix dependence (Xe, CH$_4$) of the spectra of $Ru(CO)_2(Me_2PC_2H_4PMe_2)$, where bulky substituents play no role, supports the conclusion that nonplanarity is an inherent property of *cis*-$Ru(CO)_2(PR_3)_2$.

(7) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. G.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94; Gaussian, Inc., Pittsburgh, 1995.
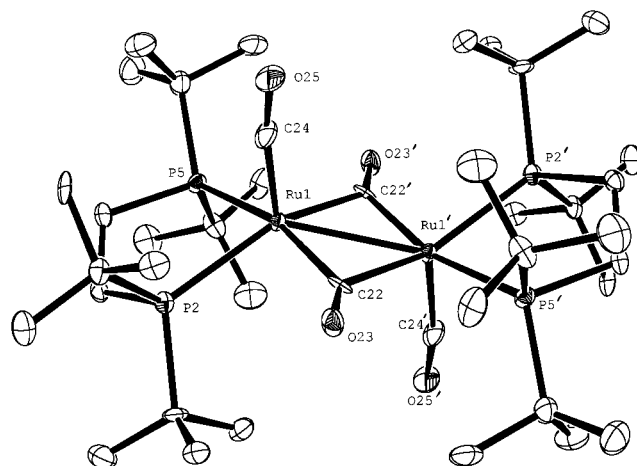(8) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: London, 1975.

(9) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.
(10) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.
(11) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.
(12) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.
(13) Höllwarth, A.; Böhme, M.; Dapprich, S.; Ehlers, A. W.; Gobbi, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 237.
(14) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.
(15) Casey, C. P.; Sakaba, H.; Hazin, P.; Powell, D. R. *J. Am. Chem. Soc.* **1991**, *113*, 8165.
(16) Church, S. P.; Grevels, F.; Kiel, G.; Kiel, W. A.; Takats, J.; Schaffner, K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 991.
(17) Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* **1974**, 2276.
(18) Haynes, A.; Poliakoff, M.; Turner, J. J.; Bender, B. R.; Norton, J. R. *J. Organomet. Chem.* **1990**, *383*, 497.