Isolable, Unsaturated Ru(0) in $Ru(CO)_2(P^tBu_2Me)_2$: Not Isostructural with Rh(I) in $Rh(CO)_2(PR_3)_2^+$

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The chemistry of zero-valent ruthenium is primarily that of clusters (e.g., $Ru_3(CO)_{12}$ and its derivatives). Exceptions include $Ru(CO)_5$ and its derivatives and also a small number of (arene)-RuL_2 species.[1] Without exception,[2] isolable Ru(0) complexes are coordinatively saturated, and flash photolysis and matrix isolation methods are necessary to create and study short-lived transient 16-electron Ru(0) species.[3–5] We present here the synthesis, X-ray structure, and bonding properties of $Ru(CO)_2L_2$ ($L = P^tBu_2Me$). This work also serves to broaden the significance of the unusual (neither tetrahedral nor planar) structure of the matrix-isolated species $Fe(CO)_4$.[6]

Reduction of *cis,cis,trans*-$RuCl_2(CO)_2L_2$[7] in THF with stoichiometric activated Mg turnings is complete in 20 h, with a color change from colorless to deep red. Recrystallization from cold pentane gives an 80% yield of **I**. Complex **I** shows one

$$RuCl_2(CO)_2L_2 + Mg \xrightarrow{25\ ^\circ C} \underset{\textbf{I}}{Ru(CO)_2L_2} + MgCl_2 \quad (1)$$

$^{31}P\{^1H\}$ NMR signal, one virtual triplet for ^tBu protons, and one virtual triplet for its P–Me hydrogens. These indicate that the phosphine ligands are equivalent and transoid. Its CO stretching vibrations (1831 and 1902 cm^{-1}) are consistent with a low oxidation state of ruthenium. The observation of two infrared allowed bands indicates that the carbonyl ligands are *not* trans.

The solid-state (X-ray) structure determination[8] of $Ru(CO)_2L_2$ reveals a structure (Figure 1) markedly different from the planar isoelectronic species $Rh(CO)_2L'_2{}^+$ ($L' = TMP = P[2,4,6\text{-}C_6H_2(OMe)_3]_3$)[9] and $Rh(CNR)_2L_2^+$ ($R = CH_2CMe_3$, $L = P^iPr_3$).[10] The bulky phosphines are nearly *trans* ($\angle P{-}Ru{-}P = 165.56(8)^\circ$), but the carbonyl ligands are far from the *trans* situation within an angle C–Ru–C of 133.3(4)°. This structure is retained in solution: Determination of the angle between the two CO vectors based on the intensities of the ν(CO) bands at 1902 and 1831 cm^{-1} in aliphatic hydrocarbon solvent gives a value of 130°. The Ru–CO unit is significantly bent ($\angle Ru{-}C{-}O = 168.2(8)^\circ$ and $168.7(7)^\circ$) in a cisoid mode. The molecule is better viewed as a fragment of the trigonal bipyramid $Ru(CO)_3L_2$ from which an equatorial carbonyl ligand has been removed with no significant relaxation of the geometry of the remaining atoms bonded to Ru. There are no agostic interactions; the shortest Ru–H distance (to a ^tBu hydrogen) is 2.7 Å. The structure has features in common with that of $Fe(CO)_4$ which is a distorted tetrahedron with angles of 120° and 145° at the metal.[6] However, the Fe complex is a spin triplet while $Ru(CO)_2L_2$ is a singlet species, as are $Ru(CO)_4$[11] and $Ru(L_2)_2$ (L_2 = dmpe).[3] Distortion away from planar geometry was predicted (EHT studies) to be facile for d^8 ML_4 with π-acceptor ligands.[12] The structure of $Ru(CO)_2L_2$ is closely related to that of $Ru(CO)_4$[5], which has been calculated to have C_{2v} symmetry[11] with C–Ru–C angles equal to 135° and 172°.

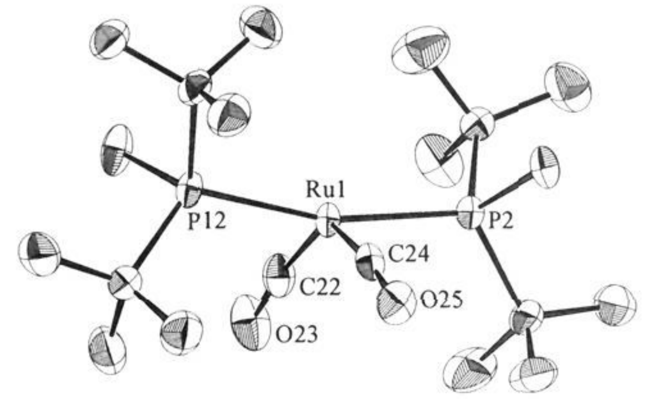
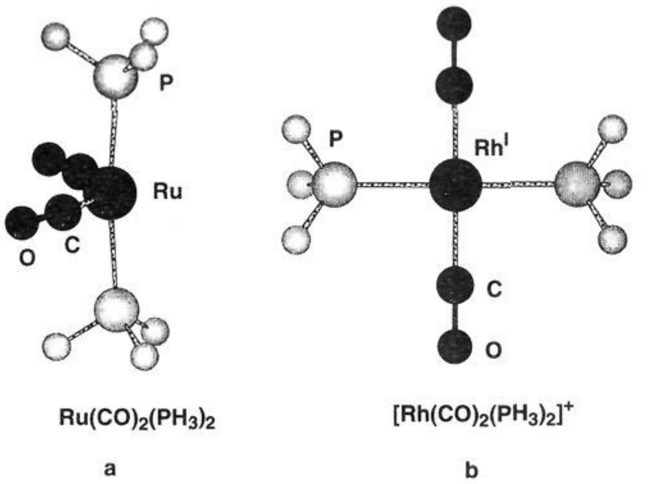


Figure 1. ORTEP drawing of $Ru(CO)_2(P^tBu_2Me)_2$, showing selected atom labeling.



$Ru(CO)_2(PH_3)_2$
a

$[Rh(CO)_2(PH_3)_2]^+$
b

Figure 2. MP2 optimized structures of $Ru(CO)_2(PH_3)_2$ (a) and $[Rh(CO)_2(PH_3)_2]^+$ (b).

The model complex $Ru(CO)_2(PH_3)_2$ has been fully optimized (Figure 2a) by core potential *ab initio* methods at the RHF/MP2 level with basis sets of triple and double ζ quality for the metal and P, C, and O, respectively,[13] using the Gaussian 92

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(1) Bennett, M. A.; Bruce, M. I.; Matheson, T. W. *Compr. Organomet. Chem.* **1982**, *4*, 691.

(2) We exclude from consideration compounds containing a π-donor ligand, e.g., $RuCl(NO)(PPh_3)_2$: Stiddard, M. H. B.; Townsend, R. E. *Chem. Comm.* **1969**, 1372.

(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) $Ru(styrene)_2(PPh_3)_2$ represents a standard for comparison, but one of the styrene rings shows evidence of η^3 character. See: Chaudret, B. N.; Carrondo, M.; Cole-Hamilton, D. J.; Skapski, A. C.; Wilkinson, G. J. *J. Chem. Soc., Chem. Commun.* **1978**, 463. $Ru(CO)_2(PMe_3)_2$ has been produced and studied by photolysis and matrix isolation methods. We thank R. J. Mawby, R. N. Perutz, and M. K. Whittlesey (*Organometallics* **1995**, *14*, 3268) for communicating their results. We have earlier reported a 14-electron Ru(0) complex, $Ru(CO)(P^tBu_2Me)_2$. See: Heyn, R. H.; Caulton, K. G. *J. Am. Chem. Soc.* **1993**, *115*, 3354. In a full paper in preparation, we show that this species is in fact the 16-electron Ru(II) molecule $Ru(H)_2(CO)(P^tBu_2Me)_2$, whose hydride ligands are extremely broad in the ^1H NMR spectrum above −95 °C.

(5) Bogdan, P. L.; Weitz, E. *J. Am. Chem. Soc.* **1989**, *111*, 3163.

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(8) Crystallographic data (−171 °C): $a = 11.601(3)$ Å, $b = 14.320(3)$ Å, $c = 15.404(3)$ Å, $\beta = 107.65(1)^\circ$, with $Z = 4$ in space group $P2_1/n$. $R(F) = 0.0666$ using 2941 reflections with $F > 3\sigma(F)$ and anisotropic thermal parameters on all non-hydrogen atoms. There is some evidence that the crystal employed had a small fragment of an impurity, of different orientation, attached to the primary crystal; an attempt to obtain a better X-ray data set is planned.

(9) Haefner, S. C.; Dunbar, K. R.; Bender, C. *J. Am. Chem. Soc.* **1991**, *113*, 9540.

(10) Jones, W. D.; Hessel, E. T. *Organometallics* **1990**, *9*, 718.

(11) Ziegler, T. *Inorg. Chem.* **1986**, *25*, 2721. Li, J.; Schreckenbach, G.; Ziegler, T. *J. Am. Chem. Soc.* **1995**, *117*, 486.

(12) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058.

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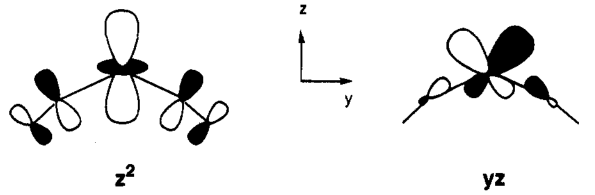
set of programs.[14] The most remarkable features of the crystal structure are closely reproduced by the calculations: ∠C−Ru−C = 132.7° and ∠Ru−C−O = 167.9° (cisoid bent). Calculations, at the same level of theory, on $Rh(CO)_2(PH_3)_2^+$ give the usual planar geometry with linear Rh−C−O (Figure 2b), in agreement with the experimental structure of $Rh(CO)_2L'_2{}^+$ (L′ = TMP). An additional important difference between the Ru(0) and Rh(I) complexes is the shorter C−O distance in the case of Rh (calculated 1.189 Å, experimental 1.125 and 1.145 Å) than in the case of Ru (calculated 1.225 Å, experimental 1.153(11) and 1.177(10) Å). In both Ru and Rh complexes, the calculated and experimental metal−ligand bond distances are in good agreement and the C−O distances are too long, as often found at this level of theory.[15] A planar Ru structure (angular constraints and optimized distances) was calculated to be 6.6 kcal/mol higher in energy than the nonplanar structure while a nonplanar Rh^I structure (at the calculated angles of $Ru(CO)_2(PH_3)_2$) is found to be 11.5 kcal/mol *less* stable than the planar structure. Of importance is the fact that, for both metals, the M−C distance shortens (by 0.04 Å for Ru and 0.03 Å for Rh) and the C−O distance lengthens (by 0.016 Å for Ru and 0.008 Å for Rh^I) upon bending the C−M−C angle. In both complexes, the M−C−O angle is calculated to be bent in the nonplanar geometry.

The main aspects of the Walsh diagram for the planar into bent transformation are established for these complexes.[16] The z^2 orbital is stabilized upon bending because of diminished overlap with the σ lone pair of CO and because back-donation into π^*_{CO} is now possible (A), as previously suggested.[12] The *xz* orbital is also stabilized by back-donation in the bent (but not in the planar) structure. The *yz* orbital (angles drawn to scale) is strongly destabilized in the bent structure because of increased overlap with the σ lone pair of CO (**B**) and diminished overlap with π^*_{CO}. However, cisoid bending of the M−C−O angle as in **B** diminishes the destabilization by minimizing the overlap between *yz* and the CO lone pair.



The preferred geometry will thus be nonplanar if the back-donation permits an efficient stabilization of z^2 and *xz* and if the destabilization of *yz* is not too large. The calculated high energy of the d orbitals (from −8 to −6 eV) in Ru(0) favors the bent structure. The stabilization by π^*_{CO} is strong due to the energetic proximity of the d orbitals while the destabilization by the σ lone pair of CO is small because of their associated large energy gap with the d orbitals. In contrast, the lower energy of the d orbitals of Rh^I (calculated −14 to −12 eV) decreases the role of the back-donation and increases the destabilization by the σ lone pair of CO. Our calculated Walsh diagrams for the Ru and Rh complexes support this description. Consistent with those ideas is the calculated significant elongation of the CO bond when going away from the planar geometry as well as the long CO bond in the case of Ru.

As proposed by Elian and Hoffmann,[12] π-acceptor ligands L are necessary for distorting ML_4 away from a square-planar structure as illustrated by the different structures of $Ru(CO)_4$,[11] $Ru(CO)_2L_2$, and RuL_4.[17] In particular, the nonplanarity of $Ru(CO)_2L_2$ is not due to the steric hindrance of the bulky phosphines since calculations using PH_3 also indicate a preference for nonplanarity. However, the distortion is more probable for high-lying d orbitals (i.e., low metal oxidation states). It thus appears that the different geometries for the two isoelectronic complexes $Ru(CO)_2L_2$ and $Rh(CO)_2L_2{}^+$ are determined by the relative energies of the d orbitals.

$Ru(CO)_2L_2$ reacts like an unsaturated, zero-valent complex, generally in the time of mixing at less than 1 atm of reagent gas pressure. It adds H_2 to give *cis,cis,trans*-$Ru(H)_2(CO)_2L_2$.[18,19] While it reacts with MeNC to give $Ru(CNMe)(CO)_2L_2$,[19] no reaction is found with isosteric MeCN (10 equiv); from these observations we can conclude that $Ru(CO)_2L_2$ is not a strong σ Lewis acid, but relies heavily on its π basicity for ligand binding. A systematic report on the reactivity of $Ru(CO)_2L_2$ will follow.

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Supporting Information Available: List of Cartesian coordinates for the RHF/MP2 optimized structures of $Ru(CO)_2(PH_3)_2$ (bent and constrained planar) and $Rh(CO)_2(PH_3)_2{}^+$ (planar and constrained bent) and crystallographic details for $Ru(CO)_2(P^tBu_2Me)_2$ and selected spectroscopic data (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[13] See supporting information for details.

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[18] This dihydride complex was also made by an independent synthesis, and it showed identical spectral parameters. This is strong evidence against the unrecognized presence of hydride ligands in "$Ru(CO)_2L_2$".

[19] Selected spectroscopic data is given as supporting information.