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Spectroscopic Assessment of the Degree of π-Stabilization of Unsaturation in $RuH(X)CO(P^tBu_2Me)_2$

Jason T. Poulton, Kirsten Folting, William E. Streib, and Kenneth G. Caulton*

Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405

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We have argued[1] that potential π-donor ligands, X, when attached to a 15-electron fragment ML_n can confer stability by forming not only an M–X σ-bond but also an X→M π-bond via lone pairs on X. We have offered structural evidence of this for the d^6 species $Ir(H)_2(OR_f)(PCy_3)_2$[1] and $Cp^*Ru(OR_f)(PCy_3)$[2] ($Cp^* = C_5Me_5$, $R_f = CH_2CF_3$). Both molecules nevertheless rapidly add nucleophiles under the mildest of conditions, so that any M/X π-donation (and thus multiple bonding) still leaves them *operationally* unsaturated.

We now report a new example of this "π-stabilized unsaturated" phenomenon in the class of molecules $RuH(X)(CO)P_2$ ($P = P^tBu_2Me$). These are synthesized from $RuH(Cl)(CO)P_2$[3] by metathesis using NaI, KOPh, LiNHPh, KOH, $KOCH_2CF_3$, $KOSiPh_3$, $KOSiMe_2Ph$, and $KOSiMe_3$. The structure[4] of the $OSiPh_3$ representative (Figure 1) shows it to have a square-pyramidal geometry with the bulky phosphines nearly linearly arrayed, but the CO and siloxide ligands bent toward one side of the basal plane, presumably away from the hydride ligand.

The CO ligand trans to the group X serves as a spectroscopic indicator of the availability of electron density at the $RuH(X)P_2$ fragment: greater back-bonding, from a more electron-rich metal center, will lower the CO stretching frequency in the infrared spectrum.[5] These data (Table I) are generally low (<1900 cm^{-1}) and reveal N- and O-based ligands to be better donors than halide. Note also that the donor power of the groups $OSiPh_xMe_{3-x}$ increases as x decreases. The CH_2CF_3 group is less electron donating than any of the silyl groups surveyed here. These data reflect a composite of σ- and π-donation by the variable ligand X. The pyridine adducts of $RuH(X)(CO)P_2$ represent another series in which the donor power of X can be evaluated (Table I).[6] For constant X, addition of pyridine decreases ν_{CO} by 13–20 cm^{-1}. Note also that the $OSiR_3$ group in the five-coordinate compound equals the composite electron-donor power of I together with pyridine. The ranking of ν_{CO} of the groups X among the six-coordinate compounds is remarkable.[7] It generally follows the sequence of ${}^5\nu_I - {}^5\nu_X$ values for the five-coordinate compounds and is constantly smaller in magnitude, but by only a few wavenumbers. The 18-electron rule would suggest that there can be *no* π-donation in the six-coordinate series. If the deficit in ${}^6\nu_I - {}^6\nu_X$ in comparison to ${}^5\nu_I - {}^5\nu_X$ is attributed wholly to π-donation by X in the five-coordinate species, the small size of the deficit suggests that such π-donation is weak. There is however an alternative to this "all or nothing" view of π-donation which arises from valence-electron counting. This procedure is based on a multicenter molecular orbital analysis of π-donation and is peculiar to the special (i.e., π-acceptor) character of CO as the ligand trans to X. The role of CO is to delocalize π-donation by X so that, even when the d^6 metal is six-coordinate, the X→Ru π-donation is not strongly destabilizing. Scheme I shows the π-interactions in the (L)Ru(H)(X) plane (the *yz* plane).[8] At left is the situation where there is no π-acceptor orbital on the ligand L. As a result, the X_π and d_{yz} orbitals (both doubly occupied) create a four-electron destabilization; with both MO's occupied, there is a net antibonding interaction. It is this which, in some cases, can make a late transition metal oxo, alkoxo, or amide ligand very nucleophilic. As shown at the right in Scheme I, the effect of a π-acid ligand L is to stabilize the HOMO and thus preserve π-donation. Note that this delocalization *can* pertain to both $RuH(X)(CO)P_2$ and $RuH(X)(py)(CO)P_2$ but that it is

Table I[a]

X	$\nu_{CO}(RuHX(CO)P_2)$, cm^{-1}	${}^5\nu_I - {}^5\nu_X$	$\nu_{CO}(RuHX(CO)(py)P_2)$, cm^{-1}	${}^6\nu_I - {}^6\nu_X$
I	1908	0	1889	0
Cl	1904	4	1884	5
OPh	1898	10	1879	10
NHPh	1898	10	1885	4
OH	1896	12	1883	6
OCH_2CF_3	1892	16	1873	16
$OSiPh_3$	1890	18	1875	14
$OSiMe_2Ph$	1888	20	1871	18
$OSiMe_3$	1886	22	1871	18

[a] FTIR spectra recorded in C_6D_6 to a precision of 0.3 cm^{-1}.

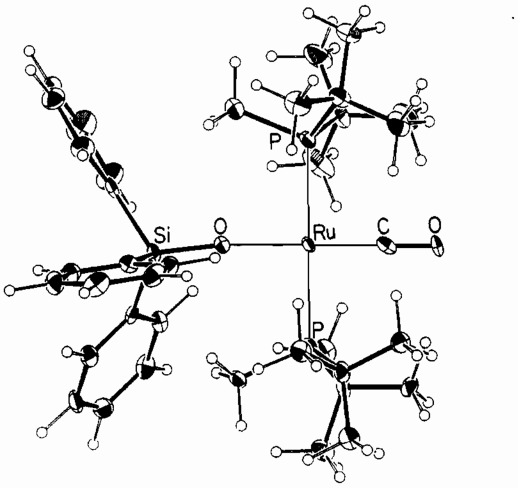

Figure 1. ORTEP drawing of $RuH(OSiPh_3)(CO)(P^tBu_2Me)_2$, showing selected atom labeling. Selected structural parameters: Ru–O, 2.057 (4) Å; Ru–P, 2.380 (2) Å; Ru–C, 1.800 (6) Å; ∠Ru–O–Si, 162.2 (3)°; ∠P–Ru–P, 177.3 (1)°; ∠C–Ru–O, 166.4 (3)°. The hydride hydrogen was not located but is concluded to project outward, toward the reader, in this view.

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(4) Crystallographic data (−160 °C) for $RuH(OSiPh_3)(CO)(P^tBu_2Me)\cdot{}^1/_4C_6H_6$: a = 11.263 (1) Å, b = 31.713 (4) Å, c = 22.311 (3) Å, and β = 100.07° with Z = 4 in space group $P2_1/n$. Using 8070 reflections with $F > 3\sigma(F)$, anisotropic thermal parameters on all non-hydrogen atoms, and hydrogens in idealized positions on carbon, $R(F)$ = 0.0541 and $R_w(F)$ = 0.0545. There are two independent molecules in the unit cell; data for these differ insignificantly, and the data for only one molecule are shown in the figure caption.

(5) The ν_{Ru-H} vibrational frequency of these compounds is generally about 2100 cm^{-1} and is broad and weak in intensity. By these criteria, the bands we report here as ν_{CO} are reliably concluded to be essentially "pure" C/O motions, unmixed with Ru–H motion.

(6) The coordination site occupied by the added pyridine is trans to the hydride. This was established by the P–H(Ru) coupling constants in the PMe_3 addition product $RuHCl(CO)(PMe_3)(P^tBu_2Me)_2$.

(7) The hydroxide and anilide cases are unusual and may be due to hydrogen bonding to the α-hydrogen by a second mole of pyridine. The origin of this anomaly is currently under investigation.

(8) An analogous argument holds for the *xy* plane if the X lone pair (of an OR or NR'_2 group) lies in the *xy* plane.

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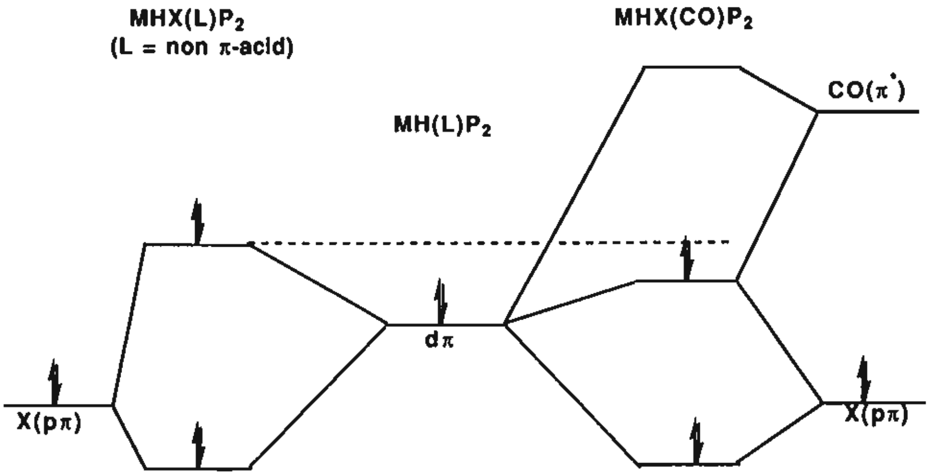
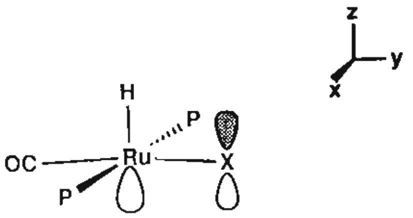
Scheme I



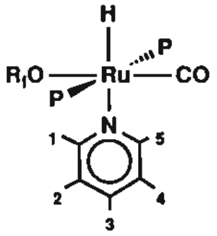
necessary for retention of X→Ru π-bonding in the latter case. "Push–pull" interaction of the mutually trans substituents X and CO enables retention of π-donation, and thus retention of *most* of the metal π-acidity, in the six-coordinate pyridine adducts. Note also that, since the overlap of the π orbital on X is not very efficient with the (mainly d_{z^2}) LUMO of a C_{4v} ML$_5$ fragment (I), the push–pull interaction in Scheme I may be mainly responsible for back-donation even in the five-coordinate RuH(X)(CO)P$_2$.



I

The pyridine binding studies cited above have also revealed several aspects of structure and dynamics in the resulting adduct:

(1) The adduct RuH(OR$_f$)(CO)(py)P$_2$ (as a representative of all X groups) manifests its sterically crowded nature by showing no rotation about the Ru–N bond (360-MHz ^{1}H NMR time scale) at −60 °C. Five-ring proton chemical shifts are resolved, requiring a structure with the pyridine ring plane not eclipsing the Ru–P bonds.



(2) The conclusion of steric crowding is reinforced by the observation that the adduct shows a ^{31}P{^{1}H} NMR AB spectrum at −85 °C. Since the ^2J(P$_A$–P$_B$) coupling constant is 306 Hz, these groups are mutually trans, and therefore their inequivalence must be due to slow rotation about the Ru–P bonds and a distribution of alkyl substituents on phosphorus which lacks mirror symmetry.

(3) As the temperature is raised above −30 °C in a solution which contains a 1:1 mixture of RuH(OR$_f$)(CO)P$_2$ and RuH(OR$_f$)(CO)(py)P$_2$, there is coalescence of the ^{31}P NMR resonances of both species, of their OCH$_2$ and their hydride resonances, and of the two α and the two β pyridine resonances of the six-coordinate species, respectively. This must therefore occur by a dissociative mechanism, which supports the idea of incomplete pyridine binding (eq 1) at higher temperatures.

$$\mathrm{RuH(OR_f)(CO)(py)P_2} \rightleftharpoons \mathrm{RuH(OR_f)(CO)P_2} + \mathrm{py} \qquad (1)$$

(4) A second (slower) ligand substitution also takes place (evident after 1 h at 25 °C in toluene) in which free pyridine converts RuH(OR$_f$)(CO)(py)P$_2$ to RuH(OR$_f$)(CO)(py)$_2$P (with production of free P^{t}Bu$_2$Me).

These last two observations are consistent with π-donation from the X ligand being a factor which promotes facile substitution chemistry via a dissociative mechanism for the normally kinetically-inert six-coordinate d^6 complexes. This effect is thus analogous to the base-catalyzed mechanism of substitution of ammine and aquo complexes of Co(III).[9]

On the basis of the results reported here, the ability to turn on and off X→M π-donation will be most fully developed in compounds (1) which contain only σ-donor ligands as companions to a single potential π-donor and (2) which have a metal orbital capable of substantial overlap with the X$_\pi$ orbital. The cases Ir(H)$_2$XP$_2$ and Cp*Ru(P)(X) meet both criteria. These both are predicted[10] to possess a trigonal bipyramidal metal environment, and the following sketches show that even the Cp compound (B) is derived from a trigonal bipyramid. Both the structural change and the LUMO orientation in RuHX(CO)P$_2$ appear to be a result of the presence of the π-acid carbonyl ligand.

A B

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Supplementary Material Available: A listing of atomic positional parameters for RuH(OSiPh$_3$)(CO)(P^{t}Bu$_2$Me)$_2$ (1 page). Ordering information is given on any current masthead page.

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