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Notes

Contribution from the Department of Chemistry,
California State University, Northridge, California 91330,
and Istituto di Chimica Generale ed Inorganica,
Universita di Torino, Turin, Italy

Mechanism of Localized Site Exchange of Carbonyl Groups in $HM_3(CO)_9L$ Clusters

Edward Rosenberg,*[†] Claudia Barner Thorsen,[†]
Luciano Milone,[‡] and Silvio Aime[‡]

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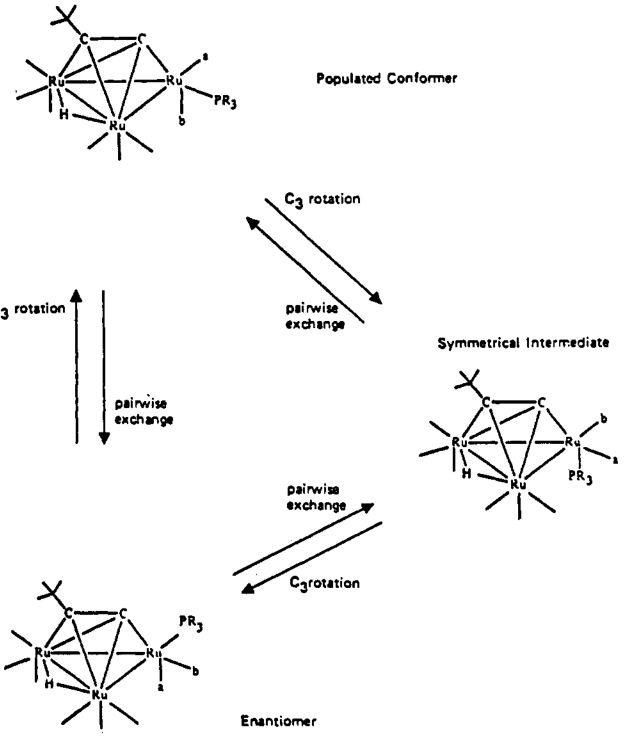
Ligand site exchange processes in transition-metal carbonyl clusters have been well investigated.[1] Although it is difficult to make mechanistic generalizations about the dynamical properties of hydride, hydrocarbon, or other bridging ligands, terminal carbon monoxide ligands do seem to follow a general pattern. In polynuclear systems having only terminal carbonyl groups, localized site exchange of magnetically inequivalent carbonyl ligands on a single metal atom is a lower energy process than exchange of carbonyls between metal atoms, a process that is thought to take place by formation of bridged intermediates.[1,2] Together the two processes completely average all carbonyl environments. The multistage nature of carbonyl site exchange in transition-metal clusters is particularly apparent in substituted carbonyl clusters where the activation energies for localized exchange processes can differ from each other by as much as they differ from the activation energy for intermetallic scrambling.

We have been studying the relationships between reactivity and ligand dynamics in organometallic clusters of the general formula $HM_3(CO)_9L$ (M = Ru, Os; L = μ_3-C_2R, μ_3-RC$=$CR'$=$CR'', μ_3-RC$=$C$=$CR'R'').[2-6] Barriers to axial-radial site exchange are significantly higher (20 kJ) at hydride-bridged metal centers and are higher yet when phosphines are substituted for carbon monoxide at the hydride-bridged metal center. Phosphine substitution at nonbridged metals, however, does not significantly alter the activation energy of localized exchange at the phosphine-substituted metal atom, suggesting that steric factors are not important in determining the activation energy for this process.

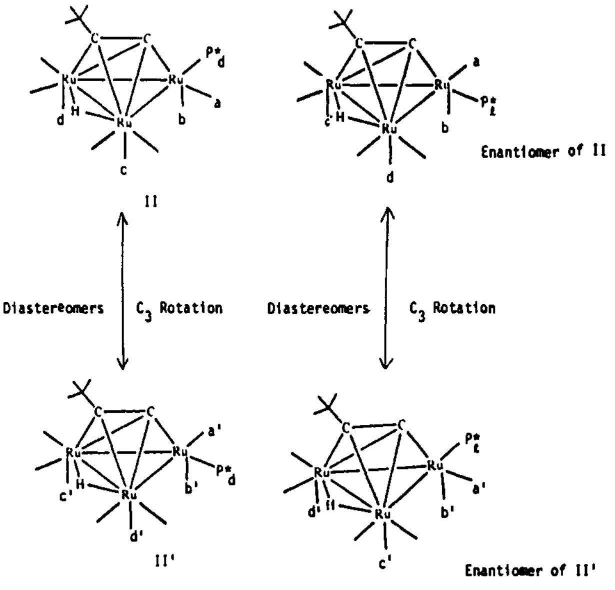
In our previous report on the synthesis, structure, and ligand dynamics of $HRu_3(CO)_8(-C_2\text{-}t\text{-}Bu)P(C_6H_5)_3$ (I), we suggested two possible pathways for axial-radial exchange at the nonbridged metal atom: (1) successive pairwise exchange of two of the three ligands; (2) simultaneous pinwheeling motion of all three ligands (a pseudo-C_3 rotation) (Scheme I). The latter process is commonly accepted, on the basis of "least motion", but, to our knowledge, has not been demonstrated. Moreover, we have recently detected pairwise exchange involving two of three carbonyl groups at both hydride-bridged and nonbridged metals.[5,6] We report here the VT ^{13}C NMR investigation of an analogue of I, $HRu_3(CO)_8[P(CH_3)(CH_2C_6H_5)(C_6H_5)]$ (μ_3-C_2-*t*-Bu) (II), in which the chiral phosphine is used as a stereochemical probe to differentiate between pairwise exchange and C_3 rotation for the localized carbonyl exchange process at the nonbridged ruthenium atom.

Substitution on the unique ruthenium atom with a chiral phosphine gives two sets of diastereometers, II and II' (Scheme II), since the cluster is intrinsically chiral when the phosphine occupies the radial position. A C_3 rotation would site-exchange b with a' and a with b' in interconverting chirality at the metal atom. The ^{13}C NMR spectrum of the diastereomeric mixture in

Scheme I. Pathways for Axial-Radial Exchange in I



Scheme II. Interconversions of Diastereomers by C_3 Rotation



the low-temperature limit should consist of four sets of doublets for the carbonyls on the unique ruthenium atom: b and b' with

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[†] California State University.

[‡] Universita di Torino.

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Table I

A. Observed Low-Temperature-Limiting $\delta(^{13}CO)^a$ Values Assignable for II

resonance	b	b′	a	a′	c^b	c′	d^b	d′
shift (223 K)	205.85	204.97	199.48	199.43	199.88	199.88	201.66	201.77
rel intens	0.32	0.68	1.0		1.0		0.32	0.68

B. Calculated Temperature-Averaged $\delta(^{13}CO)$ Values for Pairwise Exchange

$resonance^c$	a′ + b′	a + b	c + d′	d + c′
shift	202.64	202.23	201.05	200.56
$\Delta\delta$ (T, K)	0.4 (328)		0.5 (283)	

C. Calculated Temperature-Averaged $\delta(^{13}CO)$ Values for C_3 Rotation

$resonance^c$	a + b′	a′ + b	c + d′	d + c′
shift	202.90	201.90	201.05	200.56
$\Delta\delta$ (T, K)	1.0 (328)		0.5 (283)	

D. Observed Temperature-Averaged $\delta(^{13}CO)$ Values for II

resonance	aa′ + bb′ set		cc′ + dd′ set	
shift	202.5	201.3	200.7	200.2
$\Delta\delta$ (T, K)	1.2 (328)		0.5 (283)	

[a] Shifts are in ppm downfield positive from Me_4Si as measured from observed solvent peaks. [b] Assignments for d and c sets are possibly interchangeable. [c] The equilibrium constant K_{eq} = [II]/[II′] = 0.48 (223 K) was corrected for temperature, assuming $\Delta S = 0$, to a value of 0.61 at 328 K and a value of 0.56 at 283 K. These values were then used to calculate the temperature-averaged chemical shifts.

different intensities, the same coupling constant, and similar chemical shifts; a and a′ with different intensities (a = b ≠ a′ = b′), the same coupling constants, and similar chemical shifts. Axial–radial exchange by a C_3 rotation should give rise to two doublets of equal intensity in the high-temperature limit, arising from the averaging of doublets a with b′ and a′ with b. Pairwise exchange of a with b and a′ with b′ followed or preceded by pairwise exchange with phosphine would interchange CO groups within enantiomers. This averaging process also gives rise to two doublets in the high-temperature limit, but they would be of unequal intensity and of different averaged chemical shifts than those predicted by C_3 rotation. This experiment's success is contingent upon realizing resolvable chemical shift separations for a, a′, b, and b′ and different populations for each set of diastereomers. We previously reported chemical shift separations for a and b of 6.4 ppm, and we were hopeful that population differences would be significant on the basis of our previous work using this chiral phosphine with mononuclear complexes.[7]

Results and Discussion

The low-temperature-limiting ^{13}C NMR spectrum of II/II′ is obtained at 223 K (Figure 1). The carbonyl resonances can be divided into two groups by analogy with I.[3] The overlapping set of resonances from δ 190.3 to 191.8 (total relative intensity 4) is attributed to the radial carbonyls on the hydride-bridged metal atoms, and those from δ 199.4 to 205.9 (total relative intensity 4) are assigned to the three axial carbonyls and the radical carbonyl on the phosphine-substituted metal atom. More specific assignments can be made for the second group (Table IA). The two doublets centered at δ 205.85 ($^2J_{^{31}P-^{13}CO}$ = 10.4 Hz, relative intensity 0.32) and 204.95 ($^2J_{^{31}P-^{13}CO}$ = 11.0 Hz, relative intensity 0.68) are unambiguously assigned to the axial carbonyls b and b′ on the phosphine-substituted rutheniums in each of the diastereomers II and II′ (Scheme II).[1-3] The relatively large difference in δ ^{13}CO for b and b′ allows a reasonable estimate of the diastereomer populations at 223 K (K_{eq} = [II]/[II′] = 0.48). The partially resolved singlet resonances at δ 201.98 and 201.66 are in approximately the same relative intensity as b and b′ and are assigned to the axial carbonyls d and d′. The singlet resonance at δ 199.89 (relative intensity = 1.0) is assigned to the remaining set of axial carbonyls c and c′, which apparently overlap. The assignment given for d and d′ is conceivable interchangeable with that of c and c′, but it seems reasonable that the axial carbonyl set closer to the chiral phosphine (d and d′) would show a larger chemical shift difference between diastereomers. The overlapping set of resonances at δ 199.46 (relative intensity 1) is assigned to the radical carbonyls a and a′ on the phosphine-substituted ruthenium atom by direct analogy with I.[3]

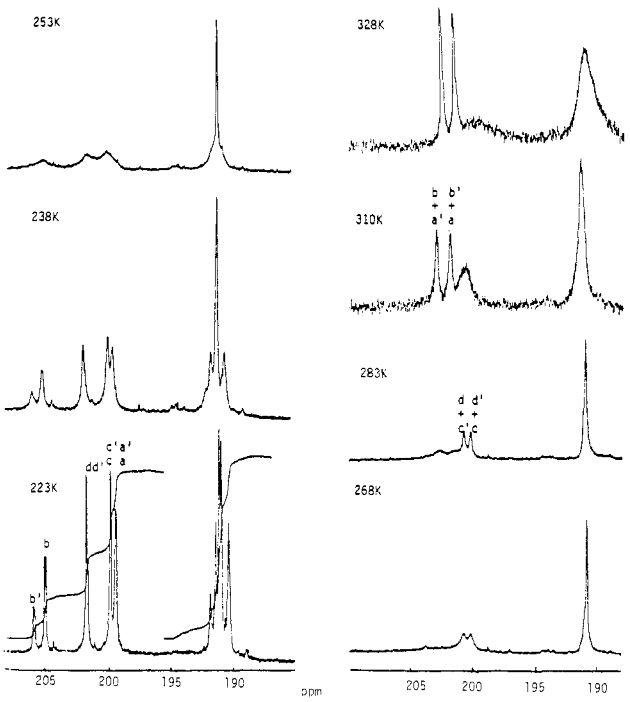

Figure 1.

The calculated high-temperature limit for pairwise exchange (a′ + b′ and a + b) and C_3 rotation (a′ + b and a + b′) from the assignments listed in Table IA are given in Table IB,C. These weighted averages were corrected for changes in population with temperature, assuming $\Delta S = 0$ for this intramolecular site exchange process. The observed temperature-averaged chemical shifts at 328 K for site exchange of the axial and radical carbonyls on the phosphine-substituted ruthenium atom (Figure 1) are given in Table ID. The observed temperature-averaged chemical shifts are in much better agreement with those calculated for C_3 rotation (Table IC) than those calculated for pairwise exchange. In addition, the two resonances observed at 328 K appear to be of equal intensity as predicted by C_3 rotation. More importantly, the observed Δδ values at 328 K (aa′–bb′ set) are in good agreement with those calculated for C_3 rotation. These results clearly differentiate between the two proposed mechanisms. The small discrepancies between the calculated and observed high-temperature-limiting chemical shifts could be due to errors in estimating the diastereomer population or to small changes in the ^{13}CO chemical shifts with temperature.[6]

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The axial-radical exchange process occurring at the phosphine-substituted ruthenium atom averages the axial carbonyls d with c′ and d′ with c into two broadened resonances of equal intensity at 283 K (Table I). The two sets of radial carbonyls on the hydride-bridged rutheniums would be expected to average into two sets of two resonances each since they are also diastereotopic when axial-radial exchange is rapid at the phosphine-substituted ruthenium atom. However, only one broadened resonance is observed at 283 K, probably due to accidental overlap and broadening of the lines by the onset of axial-radial exchange at the hydride-bridged ruthenium atoms.

Experimental Section

$Ru_3(CO)_{12}$ and $HRu_3(CO)_9(-C_2\text{-}t\text{-}Bu)$ were prepared by published procedures.[3] Deuteriodichloromethane was dried over molecular sieves (Merck). ^{13}C NMR spectra were measured on a Bruker WH-400 instrument at 100 MHz with use of a 0.1 M solution of 15-20% ^{13}CO-enriched II in CD_2C_2, 0.05 M in $Cr(acac)_3$ (Mallinckrodt). Compound II was synthesized by a procedure identical with that used for I by using $P(CH_3)(CH_2C_6H_5)(C_6H_5)$ prepared by reduction of the corresponding oxide with phenylsilane.[7] ^1H NMR (25 °C, CD_2Cl_2): δ 1.55 (9 H, s), 1.86 (3 H, d, $^2J_{^{31}P-^1H} = 11.3$ Hz), 3.51 (2 H, m), 6.68 (10 H, m), -21.1 (1 H, br). IR (KBr) ν (CO): 2075 (m), 2030 (s), 2000 (vs), 1995 (s), 1980 (s), 1940 (sh) cm^{-1}.

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Registry No. II (isomer A), 93782-56-0; II (isomer B), 93861-13-3; Ru, 7440-18-8.

Contribution from the Department of Chemistry,
University of Minnesota, Minneapolis, Minnesota 55455

Synthesis and X-ray Crystal Structure of $[(dppe)_2IrAuPPh_3](BF_4)_2$

A. L. Casalnuovo, T. Laska, P. V. Nilsson, J. Olofson,
and L. H. Pignolet*

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There has been considerable interest recently in the synthesis and structural characterization of mixed-metal cluster compounds that contain gold atoms.[1-12] Most of these clusters contain primarily carbonyl ligands bonded to the transition metals, and preparative methods have included reactions between anionic or neutral transition-metal carbonyl clusters or carbonyl hydrido clusters and monomeric gold compounds such as $Au(PR_3)Cl$ or $[Au(PR_3)]^+$. Several mixed-metal gold clusters that contain primarily phosphine ligands have been prepared by reaction of monomeric gold compounds ($AuPPh_3X$: X = Cl, NO_3) with phosphine hydrido compounds.[1,6,11] These reactions and the structures of the products have clearly shown the isolobal analogy between the hydride ligand and the $AuPR_3$ group.[8-11] See also the paper on the synthesis and structure of several new gold-iridium hydrides published in this issue of this journal.[13]

In this paper the synthesis of $[Ir(dppe)_2AuPPh_3](BF_4)_2$ (1) from the reaction of $[Ir(dppe)_2]BF_4$ with $AuPPh_3NO_3$ in the presence of HBF_4 in acetone solution is reported. This reaction gives some insight into the formation of the Au-Ir bond.

Table I. Summary of Crystal Data and Intensity Collection

Crystal Parameters	
cryst syst	monoclinic
space group	$P2_1$
cryst dimens, mm^3	0.2 × 0.3 × 0.2
cell parameters	
a, Å	11.647 (6)
b, Å	19.359 (4)
c, Å	15.952 (2)
β, deg	100.60 (2)
V, $Å^3$	3535 (3)
Z	2
d_{calcd}, g cm^{-3}	1.52
temp, °C	23
abs coeff, cm^{-1}	41.1
max, min, av transmissn factors	1.00, 0.82, 0.91
formula	$AuIrC_{70}H_{63}B_2F_8P_5$ (1)
fw	1621.9
Measurement of Intensity Data	
diffractometer	CAD 4
radiation	Mo $K\bar{\alpha}$ (λ = 0.710 69 Å) graphite monochromatized
scan type; range (2θ), deg	ω-2θ; 0-48
no. of unique reflcns measd (region)	5727 ($+h,+k,\pm l$)
no. of obsd reflcns[a]	4156 [$F_o^2 \geq 2\sigma(F_o^2)$]
Refinement by Full-Matrix Least Squares	
no. of parameters	424
R[b]	0.056
R_w[b]	0.070
GOF[b]	1.95
p[a]	0.04

[a] The intensity data were processed as described in: "CAD4 and SDP-PLUS User's Manual"; B. A. Frenz & Associates Inc.: College Station, TX, 1982. The net intensity $I = [K/\text{NPI})](C - 2B)$, where K = 20.1166(attenuator factor), NPI = ratio of fastest possible scan rate to scan rate for the measurement, C = total count, and B = total background count. The standard deviation in the net intensity is given by $[\sigma(I)]^2 = (K/\text{NPI}))^2[C + 4B + (pI)^2]$ where p is a factor used to downweight intense reflections. The observed structure factor amplitude F_o is given by $F_o = (I/Lp)^{1/2}$, where Lp = Lorentz and polarization factors. The $\sigma(I)$'s were converted to the estimated errors in the relative structure factors $\sigma(F_o)$ by $\sigma(F_o) = {}^1/_2[\sigma(I)/I]F_o$. [b] The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma(F_o)]^2$. The unweighted and weighted residuals are defined as $R = (||F_o| - |F_c||)/\Sigma|F_o|$ and $R_w = [(\Sigma w(|F_o| - |F_c|))^2/(\Sigma w|F_o|)^2]^{1/2}$. The error in an observation of unit weight (GOF) is $[\Sigma w(|F_o| - |F_c|)^2/(\text{NO} - \text{NV})]^{1/2}$, where NO and NV are the number of observations and variables, respectively.

Experimental Section

^1H and $^{31}P\{^1H\}$ NMR spectra were recorded at 300 and 120.5 MHz, respectively, with the use of a Nicolet NT-300 spectrometer. ^{31}P chemical shifts are reported in ppm relative to the internal standard trimethyl phosphate. Solvents were dried and distilled prior to use. HBF_4 was obtained from the J. T. Baker Chemical Co. as a 48-50% aqueous solution. $AuPPh_3NO_3$[14] and $[Ir(dppe)_2]BF_4$[15] were prepared as described in the literature. All manipulations were carried out under a purified N_2

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