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Potential Intermediates in Carbon Dioxide Reduction Processes. Synthesis and Structure of (μ-Formato)decacarbonyltriruthenium and (μ-Acetato)decacarbonyltriruthenium Anions

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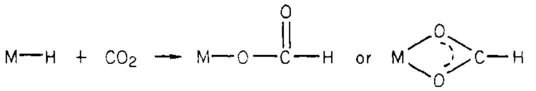
The cluster anions $[HCO_2Ru_3(CO)_{10}]^-$ and $[CH_3CO_2Ru_3(CO)_{10}]^-$ have been prepared in high yields by the reaction of $Ru_3(CO)_{12}$ with $PPN(O_2CH)$ and $PPN(O_2CCH_3)$, respectively, in refluxing THF. The formate derivative was characterized structurally and stereodynamically by X-ray crystallography and ^{13}C NMR. The salt $[N(PPh_3)_2][HCO_2Ru_3(CO)_{10}]$ crystallizes in the triclinic space group $P\bar{1}$ with the cell dimensions $a = 12.346$ (1) Å, $b = 18.878$ (2) Å, $c = 10.843$ (2) Å, $\alpha = 100.80$ (1)°, $\beta = 94.77$ (1)°, $\gamma = 108.48$ (1)°, $V = 2326.6$ Å^3, and $Z = 2$. With use of 3550 reflections having $I > 3\sigma(I)$ the structure was refined to discrepancy indices of $R_1 = 0.036$ and $R_2 = 0.042$ and a goodness-of-fit index of 1.07. The three ruthenium atoms define an isosceles triangle with the formate ligand bridging diaxially the shortest edge. The triruthenium core is symmetrically bridged with three CO ligands. A variable-temperature ^{13}C NMR study of $[PPN][HCO_2Ru_3(CO)_{10}]$ reveals the anion to be fluxional in the solution. The spectra are indicative of several dynamic processes occurring over the range −100 to +40 °C. Decarboxylation of $HCO_2Ru_3(CO)_{10}^-$ in the presence of CO was observed at elevated temperatures to provide $HRu_3(CO)_{11}^-$; the reverse reaction takes place slowly at 60 psi and more readily at 400 psi of CO_2 pressure.

Introduction

The major raw material for a C_1-based chemical industry is carbon monoxide, and a great deal of the current research efforts are designed to investigate catalysis of the reduction of CO with hydrogen.[1-3] Carbon dioxide can also serve as a convenient reagent for selected reduction processes, and interest in its use as an inexpensive source of chemical carbon has greatly intensified over the past few years.[4-10]

The reduction of carbon dioxide by means of what might *formally* be considered insertion processes represents important initial steps in the production of reduced carbon-containing molecules derived from carbon dioxide. This is most likely the case whether MH and MR symbolize homogeneous catalysts or surface metal species.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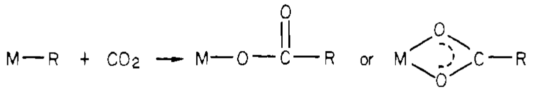
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In order to gain insight into the mechanistic aspects of CO_2 reduction processes catalyzed by transition metals, we have initiated studies aimed at fully characterizing potential intermediates in these processes, with regard to both structure and reactivity.[11-14] In view of the observations that $Ru_3(CO)_{12}$ or its derivatives are known to homogeneously catalyze the decomposition of formic acid[15] and the production of alkyl formates from CO_2, H_2, and alcohols,[16] we wish to report on the characterization of formato and acetato derivatives of the trinuclear ruthenium cluster. $Ru_3(CO)_{12}$ and $H_2Ru_4(CO)_{13}$ adsorbed on oxide supports have also been demonstrated to be effective catalysts for the methanation of carbon dioxide.[17]

Experimental Section

All manipulations were carried out either in an argon drybox or on a double manifold Schlenk vacuum line, using tetrahydrofuran and hexane which were dried by distillation from sodium benzophenone ketyl under nitrogen. $Ru_3(CO)_{12}$ and [PPN][Cl] were purchased from Strem Chemicals, Inc., and ROC/RIC Chemical Corp., respectively. $HRu_3(CO)_{11}^-$,[18] $[PPN][O_2CH]$, and $[PPN][O_2CCH_3]$[19] were prepared by the methods previously described. Infrared spectra were recorded on either a Perkin-Elmer 283B or an IBM FTIR/85 spectrometer. Proton and ^{13}C NMR spectra were determined on a Varian XL-200 spectrometer. Elemental analyses were obtained from Galbraith Laboratories, Knoxville, TN.

Preparation of (μ-Formato)decacarbonyltriruthenium Anion. A solution of $Ru_3(CO)_{12}$ (0.181 g, 0.282 mmol) and $[PPN][O_2CH]$ (0.201 g, 0.335 mmol) in 45 mL of dried, deoxygenated THF was refluxed for 1.5 h under N_2. The $[(\mu\text{-}HCO_2)Ru_3(CO)_{10}][PPN]$ complex can also be obtained in equally high yield at ambient temperatures. The solution's color turned dark red-brown immediately upon addition of THF to the substrates.

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The reaction mixture was allowed to cool to room temperature, and then the solvent was stripped off under reduced pressure. The brown residue was extracted with deoxygenated Et_2O until the extract was colorless, and the combined extracts were filtered through Celite under N_2. The volume of solution was reduced to 15 mL and the compound crystallized by slow diffusion of hexane into the cooled Et_2O solution under reduced pressure to give 0.2 g (61% yield) of orange-brown microcrystalline $[PPN][\mu\text{-}HCO_2Ru_3(CO)_{10}]$: IR (THF) 2075 (w), 2016 (s), 1992 (vs), 1960 (m, br), 1942 (m), 1813 (m), 1803 (s) cm^{-1}; ^1H NMR (CD_2Cl_2) δ (HCO_2) 6.89 (s), δ (PPN) 7.63 (m), 7.47 (m). Anal. Calcd: Ru, 25.98; C, 48.37; H, 2.67; P, 5.31. Found: Ru, 24.86; C, 46.03; H, 2.94; P, 5.29. The complex is stable up to 85 °C under N_2 as well as under CO both in the solid state and in THF. When dissolved in dimethoxyethane (DME) and heated for 20 h at 85 °C under CO, it produces $[PPN][HRu_3(CO)_{11}]$.

Preparation of (μ-Acetato)decacarbonyltriruthenium Anion. The $[PPN][\mu\text{-}CH_3CO_2Ru_3(CO)_{10}]$ complex was prepared according to the procedure described above for the formato complex: IR (THF) 2072 (w), 2020 (s), 2013 (s), 2000 (vs), 1995 (vs), 1968 (m, br), 1944 (m), 1815 (m), 1803 (m) cm^{-1}. This complex is stable in air for several hours in the solid state as well as in THF solution.

^{13}CO Enrichment Studies. ^{13}CO ligand exchange studies were performed on samples of $[HCO_2Ru_3(CO)_{10}][PPN]$, $[CH_3CO_2Ru_3(CO)_{10}][PPN]$, $[HRu_3(CO)_{11}][PPN]$, and $Ru_3(CO)_{12}$. Typically the reactions were carried out at ambient temperature in THF at concentrations of $\sim 1 \times 10^{-2}$ M. Samples were taken periodically for monitoring by infrared spectroscopy. At the beginning of each reaction and after every sample withdrawal the reaction flask was cooled in dry ice/acetone bath, evacuated, and refilled with 92% ^{13}C-enriched CO. All clusters under investigation, except $Ru_3(CO)_{12}$, were found to undergo carbon monoxide exchange.

Carboxylation of $HRu_3(CO)_{11}^-$ Anion. The CO_2 insertion into $[HRu_3(CO)_{11}][PPN]$ reaction was run in a stainless-steel high-pressure vessel. Ruthenium hydride (0.11 g, 0.098 mmol) was degassed prior to use and then dissolved in THF (10 mL; distilled from sodium ketyl). The reaction vessel was flushed with CO_2, pressurized to 60 or 400 psi at room temperature, and placed in oil bath preheated to 50 °C. The reaction mixture was stirred magnetically. After 24 h the reaction vessel was allowed to cool to room temperature and depressurized, and the liquid phase (reaction mixture was heterogeneous) was analyzed by means of IR. Spectrum revealed bands assignable to ruthenium formate (2075 (w), 2015 (s), 1997 (s), 1947 (m), 1819 (m), 1807 (m) cm^{-1}) along with an unidentified strong band at 1983 cm^{-1}.

X-ray Crystallographic Study of $[PPN][\mu\text{-}HCO_2Ru_3(CO)_{10}]$.[20] **Data Collection and Reduction.** A gold platelike crystal of $C_{47}H_{31}Ru_3NO_{12}P_2$ having approximate dimensions of 0.20 × 0.15 × 0.05 mm was mounted on a glass fiber with its long axis roughly parallel to the ϕ axis of the goniometer. Preliminary examination and data collection were performed with Mo Kα radiation (λ = 0.71073 Å) on an Enraf-Nonius CAD4 computer-controlled κ axis diffractometer equipped with a graphite crystal, incident beam monochromator.

Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $4 < 2\theta < 26°$, measured by the computer-controlled diagonal slit method of centering. As a check on crystal quality, ω scans of several intense reflections were measured: the width at half-height was 0.20° with a takeoff angle of 2.8°, indicating good crystal quality. There were no systematic absences; the space group was determined to be $P\bar{1}$ (no. 2).

A total of 6270 reflections were collected, of which 6073 were unique. As a check on crystal and electronic stability three representative reflections were measured every 41 min. The intensities of these standards remained constant within experimental error throughout data collection. No decay correction was applied.

Table I. Crystallographic Summary

A. Crystal Data	
formula	$C_{47}H_{31}Ru_3NO_{12}P_2$
fw	1166.93
cryst dimens	0.20 × 0.15 × 0.05 mm
space group	$P\bar{1}$
lattice constants	
a, Å	12.346 (1)
b, Å	18.878 (2)
c, Å	10.843 (2)
α, deg	100.80 (1)
β, deg	94.77 (1)
γ, deg	108.48 (1)
V, Å^3	2326.6
Z	2
ρ_{calcd}, g/cm^3	1.67
B. Intensity Measurements	
instrument	Enraf-Nonius CAD4 diffractometer
radiation	graphite monochromated Mo Kα (λ = 0.71073 Å)
scan type	ω-θ
scan rate, deg/min	2-20 (in ω)
scan width, deg	$0.6 + 0.350 \tan\theta$
max 2θ, deg	45.0
no. of reflctns measd	6270 total, 6073 unique
correctns	Lorentz-polarization empirical absorption (from 0.89 to 1.00)
μ, cm^{-1}	10.7
C. Structure Solution and Refinement	
solutn	direct methods
hydrogen atoms	located and refined isotropically
refinement	full-matrix least squares
minimization function	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
least-squares weights	$4F_o^2/\sigma^2(F_o^2)$
"ignorance" factor	0.050
anomalous dispersion	all non-hydrogen atoms
reflctns included	3550 with $F_o^2 > 3.0\sigma(F_o^2)$
parameters refined	710
unweighted agreement factor[a]	0.036
weighted agreement factor[b]	0.042
esd of observn of unit weight	1.07
convergence, largest shift	0.15σ
high peak in final diff map	0.69 (7) e/Å^3

[a] $R_1 = \Sigma \lVert F_o\rvert - \lvert F_c\rVert / \Sigma \lvert F_o\rvert$. [b] $R_2 = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \Sigma w F_o^2]^{1/2}$.

Structure Solution and Refinement. The structure was solved by direct methods. With use of 388 reflections (minimum E of 1.90) and 5673 relationships, a total of 16 phase sets were produced. The three Ru atoms were located from an E map prepared from the phase set with probability statistics: absolute figure of merit = 1.37, residual = 0.22, and ψ zero = 1.560. The remaining atoms were located in succeeding difference Fourier syntheses. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located and their positions and isotropic thermal parameters were refined. The structure was refined in full-matrix least squares where the function minimized was $\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$ and the weight w is defined as $4F_o^2/\sigma^2 (F_o^2)$.

Scattering factors were taken from Cromer and Waber.[21] Anomalous dispersion effects were included in F_c;[22] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[23] Only the 3550 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The final cycle of refinement included 710 variable parameters and converged (largest parameter shift was 0.15 times its esd) with unweighted and weighted agreement factors of 0.036 and 0.042, respectively. The standard

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[20] These services were performed by the crystallographic staff of Molecular Structure Corp.: Dr. M. W. Extine, Ms. R. A. Meisner, Dr. J. M. Troup, and Ms. B. B. Warrington.

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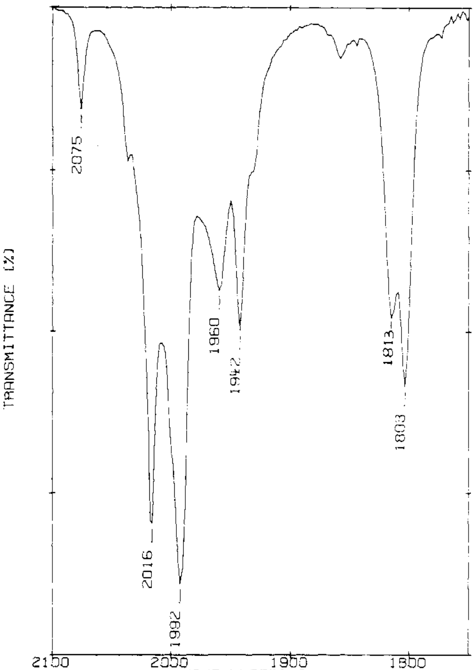

Figure 1. Infrared spectrum of $[PPN][HCO_2Ru_3(CO)_{10}]$ in tetrahydrofuran in the CO stretching region.

deviation of an observation of unit weight was 1.07. The highest peak in the final difference Fourier had a height of 0.69 e/Å^3 with an estimated error based on ΔF[24] of 0.08. Plots of $\sum w(|F_o| - |F_c|)^2$ vs. $|F_o|$, reflection order in data collection, $(\sin \theta)/\lambda$, and various classes of indices showed no unusual trends.

All calculations were performed on a PDP-11/60 based TEXRAY[25] system, which includes the Enraf-Nonius SDP and proprietary crystallographic software of Molecular Structure Corp. Table I contains a summary of crystallographic data and analysis.

Results and Discussion

Synthesis of $[PPN][CH_3CO_2Ru_3(CO)_{10}]$ and $[PPN][HCO_2Ru_3(CO)_{10}]$. These complexes result in good yield (>60%) upon refluxing $Ru_3(CO)_{12}$ and $[PPN][O_2CCH_3]$ or $[PPN][O_2CH]$ in tetrahydrofuran for 1.5 h. The solution infrared spectra in the $\nu(CO)$ region for these two ruthenium derivatives are quite similar, in both peak positions and relative intensity pattern. Figure 1 depicts such a spectrum for the formato derivative. As is apparent in Figure 1, these spectra reveal two intense vibrational modes in the bridging $\nu(CO)$ region, thus indicating at least two different environments for bridging CO groups.

These results are to be contrasted with those of Geoffroy and co-workers[26] where the analogous reaction of $Ru_3(CO)_{12}$ with [PPN][Cl] under reflux in THF provided as the product $[PPN][ClRu_4(CO)_{13}]$, which must be the consequence of $Ru_3(CO)_{12}$ declusterification. The $ClRu_4(CO)_{13}^-$ anion was shown by an X-ray structural study to possess a butterfly arrangement of the four ruthenium atoms with the chlorine bridging the two "wings" of the butterfly. Each ruthenium atom bears three terminal carbonyl ligands, and one carbonyl group bridges the two Ru atoms which constitute the hinge of the butterfly.

Crystal and Molecular Structure of $[PPN][HCO_2Ru_3(CO)_{10}]$. The final atomic positional parameters for all non-hydrogen atoms with standard deviations are compiled in Table II. The atomic labeling scheme for the

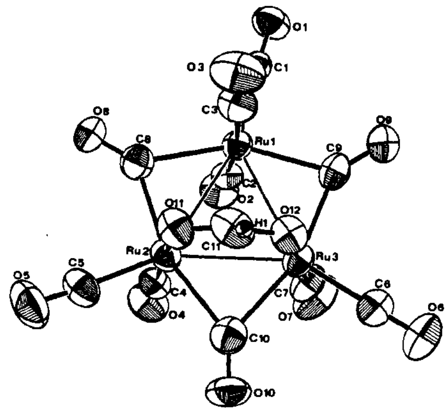

Figure 2. ORTEP drawing of the $HCO_2Ru_3(CO)_{10}^-$ anion.

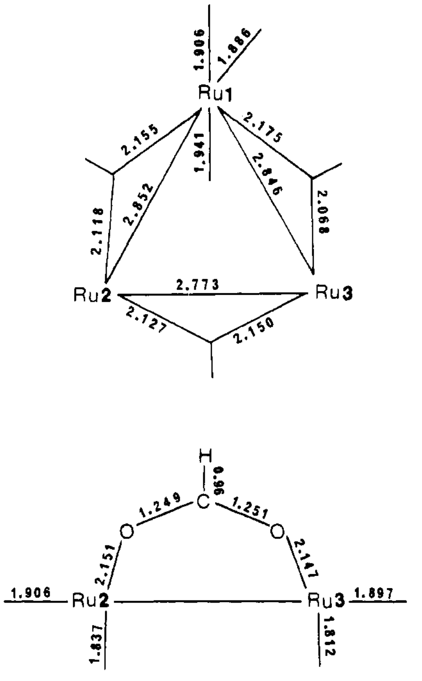

Figure 3. Summary of bond distances in the $HCO_2Ru_3(CO)_{10}^-$ anion.

anion is shown in Figure 2, whereas that for the ubiquitous cation PPN$^+$ may be found as supplementary material. Bond distances and angles for all atoms in the $HCO_2Ru_3(CO)_{10}^-$ anion are provided in Table III, with a summary of pertinent distances shown in Figure 3. The PPN$^+$ counterion was found as a well-behaved group and contained dimensions which are expected for it.[27,28] The average P-N bond length is 1.566 (6) Å, and the P-N-P angle is 151.3 (4)°; a complete listing of bond distances and angles may be found in the supplementary material.

As is illustrated in Figure 2 the anion consists of a triangular triruthenium core in which one ruthenium atom is bonded to three terminal CO groups, and the other two are bonded to two terminal CO groups and are bridged diaxially by a formate ligand. The remaining three CO ligands serve as symmetrically bridging groups for the triruthenium core. Each anion possesses approximate C_s symmetry.

The bond distance between the two ruthenium atoms bearing the bridging formate ligand is significantly shorter

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[25] TEXRAY is a trademark of Molecular Structure Corp. (1982).

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Table II. Table of Positional Parameters for all Non-Hydrogen Atoms and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Ru(1)	−0.01743 (5)	0.20011 (3)	0.43704 (6)	C(16)	0.3810 (8)	0.5858 (6)	0.4400 (9)
Ru(2)	0.15144 (5)	0.22812 (4)	0.27131 (6)	C(17)	0.3931 (7)	0.6041 (5)	0.3225 (8)
Ru(3)	0.19034 (5)	0.32899 (3)	0.50509 (6)	C(18)	0.2324 (5)	0.6920 (4)	0.0069 (7)
P(1)	0.3441 (2)	0.6650 (1)	0.1195 (2)	C(19)	0.1923 (7)	0.6079 (4)	−0.1028 (8)
P(2)	0.3759 (2)	0.8285 (1)	0.1006 (2)	C(20)	0.1101 (8)	0.5515 (5)	−0.1928 (8)
O(1)	−0.2406 (4)	0.1382 (3)	0.5390 (5)	C(21)	0.0684 (7)	0.4813 (5)	−0.1739 (9)
O(2)	−0.1426 (4)	0.2814 (3)	0.2867 (5)	C(22)	0.1031 (7)	0.4614 (4)	−0.0683 (9)
O(3)	0.0687 (5)	0.0915 (3)	0.5607 (6)	C(23)	0.1861 (6)	0.5171 (4)	0.0234 (7)
O(4)	0.0479 (5)	0.3101 (3)	0.1141 (5)	C(24)	0.4797 (5)	0.6581 (4)	0.0804 (6)
O(5)	0.2286 (5)	0.1566 (4)	0.0355 (6)	C(25)	0.5794 (6)	0.7075 (4)	0.1568 (7)
O(6)	0.3605 (5)	0.4626 (3)	0.7008 (6)	C(26)	0.6837 (6)	0.7032 (5)	0.1285 (8)
O(7)	0.0788 (5)	0.4376 (3)	0.4334 (7)	C(27)	0.6888 (6)	0.6487 (5)	0.0296 (9)
O(8)	−0.0600 (6)	0.0803 (3)	0.1808 (6)	C(28)	0.5917 (7)	0.5998 (5)	−0.0443 (9)
O(9)	0.0335 (5)	0.3017 (3)	0.7103 (5)	C(29)	0.4863 (6)	0.6031 (4)	−0.0196 (7)
O(10)	0.3715 (5)	0.3741 (4)	0.3261 (6)	C(30)	0.5090 (5)	0.8860 (3)	0.2067 (7)
O(11)	0.2449 (4)	0.1734 (3)	0.3746 (5)	C(31)	0.5045 (6)	0.9045 (4)	0.3331 (8)
O(12)	0.2792 (4)	0.2568 (3)	0.5629 (5)	C(32)	0.6026 (7)	0.9435 (4)	0.4210 (8)
N(1)	0.3303 (4)	0.7448 (3)	0.1213 (6)	C(33)	0.7053 (7)	0.9634 (4)	0.3782 (10)
C(1)	−0.1572 (7)	0.1585 (4)	0.4981 (7)	C(34)	0.7135 (6)	0.9461 (5)	0.2538 (10)
C(2)	−0.0942 (6)	0.2538 (4)	0.3443 (7)	C(35)	0.6125 (6)	0.9080 (4)	0.1661 (8)
C(3)	0.0419 (7)	0.1341 (4)	0.5131 (8)	C(36)	0.2715 (5)	0.8739 (4)	0.1348 (7)
C(4)	0.0844 (6)	0.2778 (4)	0.1748 (7)	C(37)	0.3012 (7)	0.9526 (4)	0.1715 (9)
C(5)	0.2027 (7)	0.1852 (4)	0.1235 (8)	C(38)	0.2175 (8)	0.9861 (5)	0.1950 (10)
C(6)	0.2985 (7)	0.4119 (4)	0.6277 (8)	C(39)	0.1073 (7)	0.9411 (5)	0.1813 (10)
C(7)	0.1220 (7)	0.3940 (4)	0.4589 (9)	C(40)	0.0737 (7)	0.8631 (5)	0.1507 (10)
C(8)	−0.0066 (7)	0.1371 (4)	0.2537 (8)	C(41)	0.1572 (6)	0.8300 (4)	0.1261 (8)
C(9)	0.0597 (6)	0.2894 (4)	0.6088 (8)	C(42)	0.4035 (6)	0.8332 (4)	−0.0597 (7)
C(10)	0.2887 (7)	0.3331 (4)	0.3504 (8)	C(43)	0.4567 (7)	0.7854 (4)	−0.1244 (8)
C(11)	0.2902 (7)	0.2013 (5)	0.4881 (8)	C(44)	0.4796 (8)	0.7878 (5)	−0.2430 (8)
C(12)	0.3325 (6)	0.6432 (4)	0.2734 (7)	C(45)	0.4479 (8)	0.8381 (5)	−0.3028 (8)
C(13)	0.2542 (8)	0.6618 (5)	0.3407 (9)	C(46)	0.3956 (7)	0.8841 (4)	−0.2430 (8)
C(14)	0.2414 (9)	0.6424 (7)	0.4568 (10)	C(47)	0.3737 (7)	0.8827 (4)	−0.1207 (7)
C(15)	0.3062 (10)	0.6054 (6)	0.5034 (9)				

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

(2.773 (1) Å) than the other two Ru–Ru bonds which average 2.849 (1) Å. In the neutral cluster species, (1,2-diazine)decacarbonyltriruthenium, which contains bridging CO ligands, the Ru–Ru bond bridged by the pyridazine ligand is shorter by 0.12 Å than the other two Ru–Ru distances (2.744 vs. 2.860 Å).[29] The terminal CO ligands trans to the bridging formato ligand display a sizable trans effect, where Ru–C_{eq} distances average 1.902 (10) Å and Ru–C_{ax} bond lengths are considerably shorter averaging 1.825 (10) Å or a difference of 0.077 Å. This observation is analogous to the trans metal–carbon bond shortening previously seen in monodentate formate and acetate complexes of octahedral metal carbonyls.[14,30] A corresponding trans Ru–C bond shortening was not observed in the $(C_4H_4N_2)Ru_3(CO)_{10}$ derivative. This difference in structural feature is consistent with the relative lability of the carbon monoxide ligands in these two triruthenium cluster species (vide infra). The bridging formate ligand has the anticipated geometry with equivalent C–O distances averaging 1.250 (11) Å and an O–C–O angle of 128°. Similar geometrical parameters have been noted for the formato ligand in the closely related $HOs_3(CO)_{10}(O_2CH)$ molecule recently characterized crystallographically by Shapley, Churchill, and co-workers.[31]

Reactivity Studies of the $HCO_2Ru_3(CO)_{10}^-$ and $CH_3CO_2Ru_3(CO)_{10}^-$ Anions. The formato and acetato ligands have been shown to greatly accelerate the dissociation of carbon monoxide ligands at mononuclear metal centers.[11-14,30] The availability of metal cluster prototypes possessing these O-bonded ligands naturally suggests investigations aimed at assessing the influence of these ligands on the CO lability in multinuclear metal carbonyl complexes. Studies of these types are of particular importance in view of the facile decarbonylation of these species when adsorbed on oxide supports, a process of significance in heterogeneous catalysis.[32]

The reactions defined in eq 3 and 4 were carried out in tetrahydrofuran at ambient temperature in 1 atm of ^{13}C-enriched carbon monoxide. The reactions were monitored

$$HCO_2Ru_3(CO)_{10}^- + n^{13}CO \rightleftharpoons HCO_2Ru_3(CO)_{10-n}(^{13}CO)_n^- + n^{12}CO \quad (3)$$

$$CH_3CO_2Ru_3(CO)_{10}^- + n^{13}CO \rightleftharpoons CH_3CO_2Ru_3(CO)_{10-n}(^{13}CO)_n^- + n^{12}CO \quad (4)$$

by infrared spectroscopy in the ν(CO) region (see Figure 4). Both $HCO_2Ru_3(CO)_{10}^-$ and $CH_3CO_2Ru_3(CO)_{10}^-$ were found to readily undergo carbon monoxide ligand substitution with ^{13}CO in solution. As evident in Figure 4 the reactions are >50% complete (i.e., for exchange of all bound CO groups) after only 3 h. Qualitatively the CO-labilizing ability of the acetate ligand was observed to be slightly greater than that of the formate ligand. These results are to be contrasted with the slow intermolecular exchange of carbon monoxide ligands with free CO seen in the neutral $(C_4H_4N_2)Ru_3(CO)_{10}$ derivative.[29] Parallel differences in CO-labilizing abilities have been noted in mononuclear metal carbonyl species.[33]

Variable-temperature ^{13}C NMR spectral measurements were carried out on the highly ^{13}C-enriched samples (ca. 90%) of $HCO_2Ru_3(CO)_{10}^-$ in a THF/THF-d_8 (3:1) mixture.

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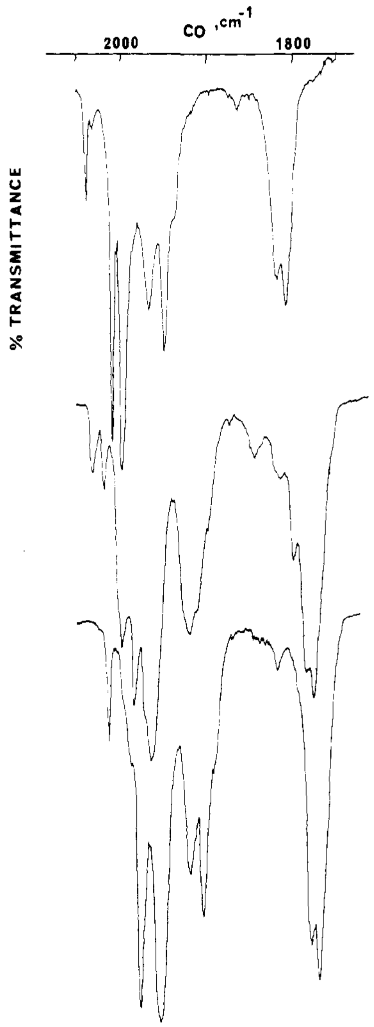

Figure 4. Infrared spectra of the exchange reaction of $HCO_2Ru_3(CO)_{10}^-$ with ^{13}C-enriched carbon monoxide at ambient temperature in tetrahydrofuran: A, at time = 0; B, after 3 h of exchange; C, after 28 h of exchange (from top to bottom).

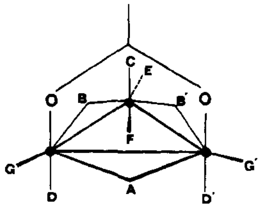

Figure 5. The structure of $HCO_2Ru_3(CO)_{10}^-$ with carbon monoxide ligands labeled in accord with the NMR peak assignment proposed in the text.

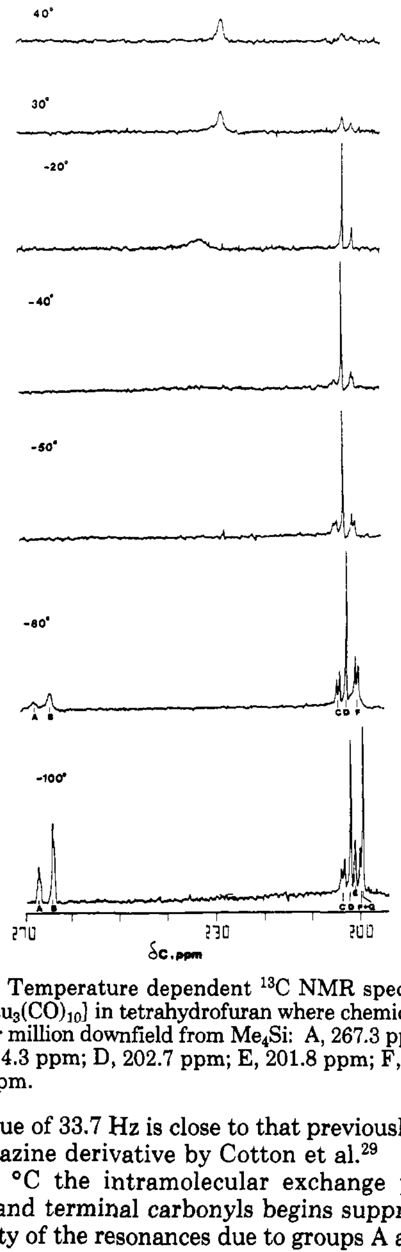

Figure 6. Temperature dependent ^{13}C NMR spectra of $[PPN][HCO_2Ru_3(CO)_{10}]$ in tetrahydrofuran where chemical shifts are in parts per million downfield from Me_4Si: A, 267.3 ppm; B, 264.3 ppm; C, 204.3 ppm; D, 202.7 ppm; E, 201.8 ppm; F, 200.8 ppm; G, 200.2 ppm.

The spectrum at -100 °C is in accord with the crystallographically determined structure (Figure 5). There are seven unequivalent groups of CO ligands in the cluster; two bridging (A and B), two equatorial (E and G), and three axial (C, D, and F) (Figure 6). The two downfield signals are due to bridging CO ligands.[18,29] The assignments of the other signals are based on changes observed during variable-temperature measurements and are similar to those seen in $(C_4H_4N_2)Ru_3(CO)_{10}$.[29] The spectrum of the anion reveals coupling between the bridging CO groups (triplet at 267.3 ppm and doublet at 264.3 ppm) with $J_{^{13}C-^{13}C}$ = 15 Hz. Coupling between the two axial CO groups bound to the unique Ru atom was also observed. This coupling is however slightly obscured in the -100 °C spectrum by the resonance of the equatorial CO groups (G) and may best be seen in the -80 °C spectrum. The $J_{^{13}C-^{13}C}$ value of 33.7 Hz is close to that previously reported for the diazine derivative by Cotton et al.[29]

At -80 °C the intramolecular exchange process of bridging and terminal carbonyls begins suppressing the multiplicity of the resonances due to groups A and B with a simultaneous coalescence of the resonances assigned to groups E and G. The exchange mechanism involves approximately coplanar six CO groups synchronously moving about the metal triangle (merry-go-round process).[34] The axial CO groups are not involved in the exchange process up to -50 °C (the only signals observed at that temperature are those of axial CO ligands C, D, and F).

The second stage of fluxionality is observed between -40 °C and room temperature. At -40 °C the signal due to C coalesces and the splitting of F is fading indicating that one of the axial CO groups on Ru(1) is entering into the terminal-bridge exchange process.[35] At -20 °C a broad signal due to the scrambling CO groups emerges at about 228 ppm. The third stage of fluxionality is observed above room temperature. At +30 °C the signals of the axial

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[35] The assignments of peaks C and F may be reversed. The provided assignment is based on literature data on related triangular metal clusters which suggest the more downfield resonance to be due to the CO ligand situated vis-à-vis the carbon bridge in complexes such as $HRu_3(CO)_{10}(COCH_3)$. Shapley, J. R.; Cree-Uchiyama, M. E.; St. George, G. M. *J. Am. Chem. Soc.* **1983**, *105*, 140. Johnson, B. F. G.; Lewis, J.; Orpen, A. G.; Raithley, P. R.; Süss, G. *J. Organomet. Chem.* **1979**, *173*, 187. Gavens, P. D.; Mays, M. J. *Ibid.* **1978**, *162*, 389.

Table III. Bond Distances (Å) and Bond Angles (deg)[a]

Bond Distances

Ru(1)-Ru(2)	2.852 (1)	Ru(2)-C(8)	2.118 (9)	O(4)-C(4)	1.134 (9)
Ru(1)-Ru(3)	2.846 (1)	Ru(2)-C(10)	2.127 (10)	O(5)-C(5)	1.128 (10)
Ru(1)-C(1)	1.886 (10)	Ru(3)-O(12)	2.147 (6)	O(6)-C(6)	1.132 (9)
Ru(1)-C(2)	1.941 (9)	Ru(3)-C(6)	1.897 (10)	O(7)-C(7)	1.174 (10)
Ru(1)-C(3)	1.906 (10)	Ru(3)-C(7)	1.812 (10)	O(8)-C(8)	1.165 (10)
Ru(1)-C(8)	2.155 (9)	Ru(3)-C(9)	2.068 (10)	O(9)-C(9)	1.175 (9)
Ru(1)-C(9)	2.175 (9)	Ru(3)-C(10)	2.150 (10)	O(10)-C(10)	1.155 (10)
Ru(2)-Ru(3)	2.773 (1)	O(1)-C(1)	1.137 (9)	O(11)-C(11)	1.249 (11)
Ru(2)-O(11)	2.151 (6)	O(2)-C(2)	1.129 (9)	O(12)-C(11)	1.251 (11)
Ru(2)-C(4)	1.837 (10)	O(3)-C(3)	1.149 (10)	C(11)-H(1)	0.96 (7)
Ru(2)-C(5)	1.906 (10)				

Bond Angles

Ru(2)-Ru(1)-Ru(3)	58.25 (2)	Ru(3)-Ru(2)-C(4)	98.6 (3)	O(12)-Ru(3)-C(10)	86.0 (3)
Ru(2)-Ru(1)-C(1)	161.3 (3)	Ru(3)-Ru(2)-C(5)	152.1 (3)	C(6)-Ru(3)-C(7)	89.7 (4)
Ru(2)-Ru(1)-C(2)	86.6 (2)	Ru(3)-Ru(2)-C(8)	109.4 (3)	C(6)-Ru(3)-C(9)	101.8 (4)
Ru(2)-Ru(1)-C(3)	94.7 (3)	Ru(3)-Ru(2)-C(10)	49.9 (3)	C(6)-Ru(3)-C(10)	98.4 (4)
Ru(2)-Ru(1)-C(8)	47.6 (3)	O(11)-Ru(2)-C(4)	174.2 (3)	C(7)-Ru(3)-C(9)	90.2 (4)
Ru(2)-Ru(1)-C(9)	104.4 (3)	O(11)-Ru(2)-C(5)	86.8 (3)	C(7)-Ru(3)-C(10)	93.2 (4)
Ru(3)-Ru(1)-C(1)	139.9 (3)	O(11)-Ru(2)-C(8)	92.2 (3)	C(9)-Ru(3)-C(10)	159.5 (4)
Ru(3)-Ru(1)-C(2)	92.2 (2)	O(11)-Ru(2)-C(10)	87.4 (3)	Ru(2)-O(11)-C(11)	122.1 (6)
Ru(3)-Ru(1)-C(3)	95.5 (3)	C(4)-Ru(2)-C(5)	89.0 (4)	Ru(2)-C(5)-O(5)	176.7 (9)
Ru(3)-Ru(1)-C(8)	105.8 (3)	C(4)-Ru(2)-C(8)	92.3 (4)	Ru(3)-C(6)-O(6)	177.7 (8)
Ru(3)-Ru(1)-C(9)	46.3 (3)	C(4)-Ru(2)-C(10)	89.7 (4)	Ru(3)-C(7)-O(7)	177.6 (9)
C(1)-Ru(1)-C(2)	88.0 (3)	C(5)-Ru(2)-C(8)	96.9 (4)	Ru(1)-C(8)-Ru(2)	83.7 (4)
C(1)-Ru(1)-C(3)	88.2 (4)	C(5)-Ru(2)-C(10)	103.7 (4)	Ru(1)-C(8)-O(8)	138.5 (7)
C(1)-Ru(1)-C(8)	114.2 (3)	C(8)-Ru(2)-C(10)	159.3 (4)	Ru(2)-C(8)-O(8)	137.8 (8)
C(1)-Ru(1)-C(9)	94.1 (4)	Ru(1)-Ru(3)-Ru(2)	60.99 (2)	Ru(1)-C(9)-Ru(3)	84.2 (4)
C(2)-Ru(1)-C(3)	171.7 (4)	Ru(1)-Ru(3)-O(12)	89.3 (2)	Ru(1)-C(9)-O(9)	133.8 (7)
C(2)-Ru(1)-C(8)	86.3 (3)	Ru(1)-Ru(3)-C(6)	151.0 (3)	Ru(3)-C(9)-O(9)	141.9 (7)
C(2)-Ru(1)-C(9)	99.2 (3)	Ru(1)-Ru(3)-C(7)	93.6 (3)	Ru(2)-C(10)-Ru(3)	80.8 (4)
C(3)-Ru(1)-C(8)	88.6 (4)	Ru(1)-Ru(3)-C(9)	49.5 (2)	Ru(2)-C(10)-O(10)	141.4 (8)
C(3)-Ru(1)-C(9)	88.4 (4)	Ru(1)-Ru(3)-C(10)	110.1 (3)	Ru(3)-C(10)-O(10)	137.7 (8)
C(8)-Ru(1)-C(9)	151.4 (4)	Ru(2)-Ru(3)-O(12)	82.6 (2)	O(11)-C(11)-O(12)	128 (1)
Ru(1)-Ru(2)-Ru(3)	60.76 (2)	Ru(2)-Ru(3)-C(6)	146.6 (3)	O(11)-C(11)-H(1)	129 (4)
Ru(1)-Ru(2)-O(11)	88.6 (2)	Ru(2)-Ru(3)-C(7)	98.9 (3)	O(12)-C(11)-H(1)	102 (4)
Ru(1)-Ru(2)-C(4)	97.1 (3)	Ru(2)-Ru(3)-C(9)	110.3 (2)	Ru(3)-O(12)-C(11)	123.3 (6)
Ru(1)-Ru(2)-C(5)	145.1 (3)	Ru(2)-Ru(3)-C(10)	49.2 (3)	Ru(1)-C(1)-O(1)	175.5 (8)
Ru(1)-Ru(2)-C(8)	48.7 (3)	O(12)-Ru(3)-C(6)	87.7 (3)	Ru(1)-C(2)-O(2)	176.4 (8)
Ru(1)-Ru(2)-C(10)	110.6 (3)	O(12)-Ru(3)-C(7)	177.1 (3)	Ru(1)-C(3)-O(3)	174.4 (9)
Ru(3)-Ru(2)-O(11)	83.4 (2)	O(12)-Ru(3)-C(9)	91.6 (3)	Ru(2)-C(4)-O(4)	176.9 (8)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

groups (D and F) broaden and collapse at +40 °C with a concomitant sharpening of the average signal at 227.6 ppm.

In an analogous experiment CO ligand exchange involving the $HRu_3(CO)_{11}^-$ anion was carried out for comparison with the carboxylate derivatives. $HRu_3(CO)_{11}^-$ was indeed observed to exchange CO ligands under conditions identical with those above at a comparable rate. By way of contrast $Ru_3(CO)_{12}$ was found under identical conditions *not* to commute bound CO with free CO in solution over an extended period (>2 days). These results are consistent with the observations by Shore and co-workers[36] where $Ru_3(CO)_{12}$, *in the presence of KH*, underwent CO exchange with ^{13}CO in solution (eq 5). Not only does ^{13}CO displace

$$KH + Ru_3(CO)_{12} \rightleftarrows [K][HRu_3(CO)_{11}] + CO \quad (5)$$

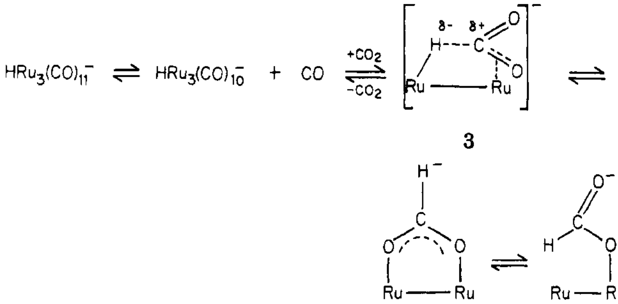
hydride to afford ^{13}C-enriched $Ru_3(CO)_{12}$, but also as we have demonstrated here, $HRu_3(CO)_{11}^-$ can undergo CO ligand exchange on the same time scale as hydride displacement.

In a reaction of perhaps more importance to the CO_2 reduction process $HCO_2Ru_3(CO)_{10}^-$ decarboxylates in the presence of carbon monoxide at elevated temperatures in aprotic solvents (eq 6). The reverse reaction, carboxyl-

$$HCO_2Ru_3(CO)_{10}^- + CO \rightleftarrows HRu_3(CO)_{11}^- + CO_2 \quad (6)$$

ation, of $HRu_3(CO)_{11}^-$ occurs as well to provide the μ-$HCO_2Ru_3(CO)_{10}^-$ derivative. This process takes place only slowly at 60 psi pressure but more readily at 400 psi of carbon dioxide pressure. Analogous carboxylation and decarboxylation processes involving dimeric metal formate derivatives have been previously reported.[37-39]

Scheme I



In all of these instances of decarboxylation involving bridging formate derivatives it has not been defined as to whether the metal–hydrogen bond forming process occurs at the same metal center that contains the bound formate ligand (1) or at adjacent metal centers (2). It is enticing

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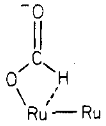

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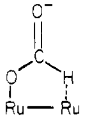

2

to propose a process (Scheme I) that proceeds via a transition state (**3**), which is consistent with the available data, e.g., CO loss from $HRu_3(CO)_{11}^-$ is faster than CO_2 insertion. Indeed the insertion reaction described in Scheme I is retarded in the presence of a carbon monoxide atmosphere. However, intimate mechanistic detail of reaction 6 must await further experimental observations. These experiments are presently in progress in our laboratories.

Acknowledgment. The financial support of the National Science Foundation through Grant CHE 80-09233 is greatly appreciated.

Registry No. [PPN][μ-$HCO_2Ru_3(CO)_{10}$], 86528-72-5; [PPN][μ-$CH_3CO_2Ru_3(CO)_{10}$], 86528-74-7; [$HRu_3(CO)_{11}$][PPN], 71936-70-4; $Ru_3(CO)_{12}$, 15243-33-1; CO_2, 124-38-9; CO, 630-08-0.

Supplementary Material Available: Lists of structure factor amplitudes, tables of thermal parameters, positional parameters for hydrogen atoms, and bond lengths and angles in the cation, and ORTEP drawing of cation PPN (20 pages). Ordering information is given on any current masthead page.

Reaction of Thioesters and Thiolactones with Cyclopentadienylmetal Dicarbonyl Dimers

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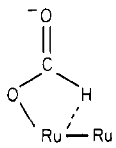
Complexes containing a metal-metal triple bond, $(RC_5H_4)_2M_2(CO)_4$ (R = H, CH_3; M = Mo, W), react with thioesters and thiolactones to give compounds of type (thioester or thiolactone) $M_2(CO)_4(C_5H_4R)$. Analytical and spectral data, together with an X-ray analysis of the (thiobutyrolactone)molybdenum complex, revealed that the sulfur is bonded to both molybdenum atoms and that a semibridging carbonyl group is present. There is no evidence for bonding of the oxygen, of the organic ligand, to a metal atom. Crystal data for $[(C_5H_5)_2Mo_2(CO)_4(SC_4H_6O)]$: tetragonal space group $P4_2bc$, a = 19.872 (3) Å, c = 9.643 (2) Å, V = 3808.0 Å^3, Z = 8. The intensities of 1384 reflections with $I > 2.3\sigma(I)$, collected by counter methods with Mo Kα radiation, were used in the least-squares refinement. Final R_F = 0.021 and R_{wF} = 0.025. The bridgehead C atom is bonded to one Mo atom while S bridges between both Mo atoms: Mo(1)–Mo(2) = 3.138 (1) Å, Mo(2)–C = 2.235 (6) Å, Mo(1)–S = 2.402 (1) Å, Mo(2)–S = 2.385 (2) Å, and S–C = 1.807 (6) Å. There is a semibridging carbonyl group: Mo(2)–C(21) = 1.944 (6) Å, Mo(1)···C(21) = 2.764 (8) Å, and Mo(2)–C(21)–O(21) = 162.7 (7)°.

Introduction

Much work has been done on the chemistry of metal–metal multiple bonds, including complexes bearing carbonyl ligands.[2,3] Some recent examples include the reaction of the in situ generated cyclopentadienylmolybdenum (or tungsten) dicarbonyl dimer **1** which contains a triple bond between the metal atoms, with $M(CO)_2(NO)(C_5H_5)$ (M = Mo, W) affording homonuclear and heteronuclear metal cluster nitrides **2**;[4] with α-halo ketones to give the dehalogenated ketone **3** and the organomolybdenum tricarbonyl halide **4**;[5] and with nitro compounds to form high oxidation state molybdenum and tungsten complexes having bridging and terminal oxygen ligands (**5**).[6]



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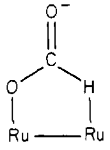

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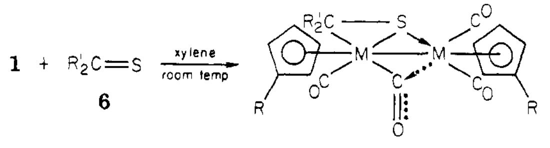

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In 1979, one of us[7] reported a new class of thione complexes (**7**) obtained by the reaction of **1** with thioketones **6** under mild conditions. Such complexes have the thione function bonded to one metal atom, with the sulfur donor bound to the other metal atom, and a semibridging carbonyl group is also present. It seemed of interest to learn the effect of a heteroatom on (a) the course of the complexation reaction and (b) the bonding parameters assuming complexes of structural type **7** were formed. Therefore, a series of thioesters and thiolactones were treated with the metal–metal triple bonded complexes **1**. A previous study in the area of orthometalation showed

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(1) (a) University of Ottawa. (b) Simon Fraser University.

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