

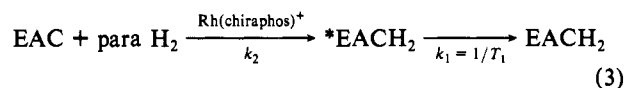
obviating accurate quantitation of this polarized proton. For each FID, eight scans were collected within 12 s using a 30° observe pulse; a 20-s delay was incorporated between each FID. The integral area¹³ in the polarized resonances was quantified every 32 s for 448–480 s. Polarization measured after the sample was removed, reshaken, and reinserted into the spectrometer showed reproducible decay of the polarization intensity. Samples containing 2.1 mM **1** exhibited exponential decay of polarization intensity during the time of NMR observation. Concomitant disappearance of the NMR-active ortho H₂¹⁴ resonance was also noted. Polarization curves from samples containing higher catalyst concentrations exhibited more rapid decay of polarized signal. The rate constants of polarization decay (k_{obsd}) were determined by fitting the polarization intensity curves to a decaying exponential function. A plot of k_{obsd} vs total catalyst concentration produced a straight-line graph with slope of 0.87 M⁻¹ s⁻¹ and intercept at the origin. This number compares favorably with Halpern's reported value of 1.6 M⁻¹ s⁻¹.¹¹

A striking feature of our study was that the time dependence of polarization agreed with the rate of hydrogenation, as measured by integrating the unpolarized acyl methyl resonance of EACH₂ versus time (shown in Table I under k_2' (PROD)). In the regime of these experiments where EAC is present in excess, H₂ is the limiting reagent. Thus the rate equation for EAC hydrogenation

$$\text{rate} = \frac{k_2 K [\text{Rh}]_{\text{T}} [\text{EAC}] [\text{H}_2]}{(1 + K [\text{EAC}])} \approx k_2' [\text{H}_2] \quad (2)$$

(eq 2),¹⁵ where $[\text{Rh}]_{\text{T}}$ is the total catalyst concentration, K is the equilibrium constant between Rh(chiraphos)⁺ + free EAC and **2**, and k_2 is the rate constant for the hydrogenation of **2**, simplifies to a first-order rate expression in $[\text{H}_2]$ with $k_2' = k_2 [\text{Rh}]_{\text{T}}$.

A simple analysis of the time dependence of PHIP reveals its relationship to the rate of hydrogenation. For PHIP to occur, H₂ enriched in the para spin state is required. The factors influencing the time dependence of polarization in PHIP include the following: (1) proton spin-lattice relaxation, (2) cross-relaxation, (3) the rate of chemical reaction to produce polarized product, (4) promotion of para H₂-ortho H₂ interconversion, and (5) para-enriched H₂ diffusion from the gas phase into solution within the NMR tube. Point **2** is removed from consideration by combining the integrals of H_a and H_b in our data analysis. It is clear from T_1 values for H_a and H_b determined by the inversion-recovery method as 1.7 s ($1/T_1 = k_1 = 0.57 \text{ s}^{-1}$) that polarization lasts far longer than would be predicted on the basis of spin-lattice relaxation alone. This means that newly polarized product is formed in the probe as "older" product undergoes rapid relaxation, eq 3, leading to eqs 4 and 5 for the time dependence of the concentration of polarized product where $A_0 = \{k_2' / (k_1 - k_2')\} [\text{para H}_2]_0$. When $k_1 \gg k_2'$, contribution from the second



$$\frac{d[\text{*EACH}_2]}{dt} = k_2' [\text{para H}_2] - k_1 [\text{*EACH}_2] \quad (4)$$

$$[\text{*EACH}_2] = A_0 \exp(-k_2' t) - (A_0 - [\text{*EACH}_2]_0) \exp(-k_1 t) \approx A_0 \exp(-k_2' t) \quad (5)$$

term of the time dependence of polarized product rapidly approaches zero, and beyond this initial period, $[\text{*EACH}_2]$ behaves as a simple exponential with rate constant k_2' . Thus $[\text{*EACH}_2]$,

(12) CD₃OH occurs at 4.78 ppm at 25 °C relative to CD₂HOD (3.30 ppm).

(13) For NMR signals that exhibited emission and absorption, the square root of the power spectrum of these integrals was used as a measure of signal intensity.

(14) Para H₂ has no magnetic moment and is therefore silent in NMR spectroscopy.

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which depends on the amount of para-enriched H₂ in solution, reflects the rate of reaction.

The catalytic aspect of eq 1 ensures that significant amounts of polarized product are generated during the time period of observation. The time dependence of polarization thus serves as an accurate monitor of the synthesis of newly polarized product even in light of rapid spin-lattice relaxation. This implies that the ROCHESTER technique can be applied to a wide range of hydrogenations that display PHIP to yield kinetic information from quantitation of enhanced resonances.

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Opening of Metal Carbonyl Cluster Complexes by Ligand Addition. Synthesis and Structural Characterization of Os₃(CO)₁₁(μ-CNCF₃)₂, a Stabilized Derivative of the Hypothetical Complex Os₃(CO)₁₃

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The mechanisms of ligand addition and substitution are fundamental to understanding the reactivity of metal carbonyl cluster complexes.¹ The trinuclear metal carbonyl cluster complexes of the iron subgroup M₃(CO)₁₂ (M = Fe, Ru, Os) are the starting points for the study of a wide range of today's transition metal clusters complexes.¹ Investigations of ligand substitution and cluster fragmentation reactions of these complexes have revealed two-term rate expressions that have been interpreted in terms of dissociative and associative mechanisms, respectively.² A variety of structures having a cleaved metal-metal bond have been proposed to explain the intermediates anticipated by the addition of a ligand to these complexes.^{2,3} In an attempt to prepare the complex Os₃(CO)₁₁(CNCF₃), we accidentally obtained the addition product Os₃(CO)₁₁(μ-CNCF₃)₂ (**1**), a stabilized derivative of the unknown complex Os₃(CO)₁₃ and a possible structural model for the ligand addition products of other reactions with the M₃(CO)₁₂ cluster complexes.

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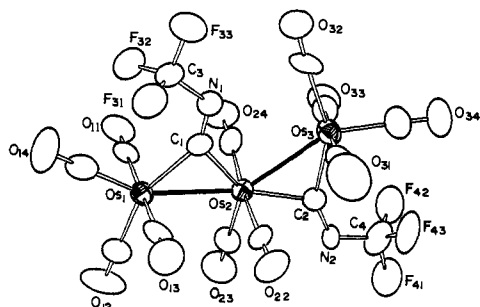
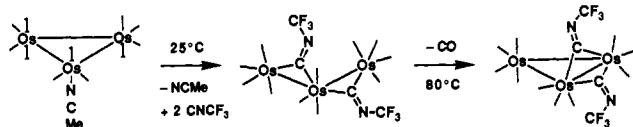


Figure 1. ORTEP diagram of $\text{Os}_3(\text{CO})_{11}(\mu\text{-CNCF}_3)_2$ (**1**). Selected interatomic distances (angstroms) and angles (degrees): $\text{Os}(1)\text{-Os}(2) = 2.859$ (1), $\text{Os}(2)\text{-Os}(3) = 2.847$ (1), $\text{Os}(1)\text{-C}(1) = 2.07$ (2), $\text{Os}(2)\text{-C}(1) = 2.13$ (2), $\text{Os}(2)\text{-C}(2) = 2.10$ (2), $\text{Os}(3)\text{-C}(2) = 2.01$ (2); $\text{Os}(1)\text{-Os}(2)\text{-Os}(3) = 140.39$ (4).

Scheme I



Complex **1** was prepared in 35% yield together with a small amount of the new compound $\text{Os}_3(\text{CO})_{10}(\mu\text{-CNCF}_3)_2$ (**2**) (4% yield) from the reaction of $\text{Os}_3(\text{CO})_{11}(\text{NCMe})$ with an excess CNCF_3 in CH_2Cl_2 solvent at 25 °C for 5 min.^{4,5} Both complexes were characterized by IR and ^{19}F NMR spectroscopy and by single-crystal X-ray diffraction analyses.^{6,7} An ORTEP drawing of the molecular structure of **1** is shown in Figure 1. The molecule was found to consist of an *open* triosmium cluster with CNCF_3 ligands bridging each of the two metal-metal bonds. The CNCF_3 ligands are structurally inequivalent. This inequivalence was also observed in solution at -34 °C by ^{19}F NMR spectroscopy, but as the temperature is raised, the resonances broaden and coalesce ($T_c = 283$ K) due to a dynamical averaging process and are observed as a broad singlet at $\delta -60.2$ ppm at 296 K. Compound **1** was formed by the displacement of the labile NCMe ligand of the $\text{Os}_3(\text{CO})_{11}(\text{NCMe})$ and the addition of two molecules of CNCF_3 . The sequence of these two steps has not yet been established. The complex is electron precise with two metal-metal bonds as expected for a 50-electron configuration. The strong preference of CNCF_3 ligands to adopt bridging coordination modes

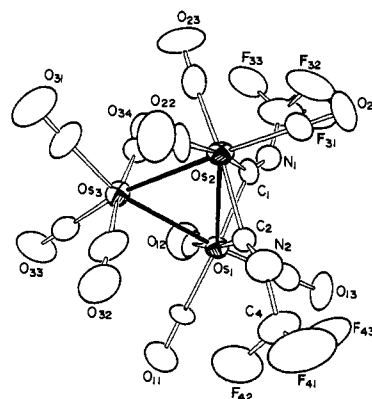


Figure 2. ORTEP diagram of $\text{Os}_3(\text{CO})_{10}(\mu\text{-CNCF}_3)_2$ (**2**). Selected interatomic distances (angstroms): $\text{Os}(1)\text{-Os}(2) = 2.742$ (1), $\text{Os}(1)\text{-Os}(3) = 2.850$ (1), $\text{Os}(2)\text{-Os}(3) = 2.850$ (1), $\text{Os}(1)\text{-C}(1) = 2.15$ (2), $\text{Os}(2)\text{-C}(1) = 2.11$ (2), $\text{Os}(1)\text{-C}(2) = 2.11$ (2), $\text{Os}(2)\text{-C}(2) = 2.15$ (2).

has been observed previously.⁸ Indeed, it is probably the presence of the bridging CNCF_3 ligands that prevents further ligand addition and fragmentation of the cluster.

When heated to 80 °C for 5 min, compound **1** was decarbonylated and transformed to the new compound $\text{Os}_3(\text{CO})_{10}(\mu\text{-CNCF}_3)_2$ (**2**) in 87% yield.⁹ An ORTEP drawing of the molecular structure of **2** is shown in Figure 2. The molecule consists of a triangular cluster of three osmium atoms with 10 linear carbonyl ligands. As expected, the loss of one CO ligand causes the cluster to close with the formation of a metal-metal bond. The two (trifluoromethyl)isocyanide ligands bridge the same edge of the cluster, and the associated metal-metal bond distance, 2.742 (1) Å, is significantly shorter than that of the unbridged metal-metal bonds, 2.850 (1) Å. The presence of the two bridging ligands makes the structure very similar to that of $\text{Fe}_3(\text{CO})_{10}(\mu\text{-CO})_2$ and unlike that of $\text{Os}_3(\text{CO})_{12}$, which has only terminal ligands.¹⁰

A summary of the results of this study are shown in Scheme I. The opening and closing of metal-metal bonds by the addition and elimination of nucleophiles has been observed in some high nuclearity clusters and selected small clusters that are stabilized by bridging ligands,¹¹ but never before in a system of such fundamental interest as the trinuclear binary carbonyls of the iron subgroup.

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Supplementary Material Available: Tables of crystal data, positional parameters, bond distances and angles, and anisotropic thermal parameters (15 pages); tables of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

(4) On a vacuum line, 20 mL of CH_2Cl_2 was condensed into a 50-mL Schlenk tube containing 150.8 mg (0.164 mmol) of $\text{Os}_3(\text{CO})_{11}(\text{NCMe})$. The vessel was warmed to dissolve the triosmium compound. After the vessel was recooled with liquid nitrogen, 0.82 mmol of CNCF_3 was condensed into the Schlenk tube, and the mixture was then warmed to room temperature in approximately 1 min and stirred for an additional 5 min. The reaction solution changed color from yellow to orange. Finally, the Schlenk tube was flushed with nitrogen, and the solvent was evaporated under a stream of nitrogen. The residue was then washed with 30 mL of a dichloromethane/pentane solution (2:1) to yield 61 mg of $\text{Os}_3(\text{CO})_{11}(\mu\text{-CNCF}_3)_2$ as yellow powder (35%). The supernatant was evaporated to dryness and then separated by TLC (1:4, dichloromethane/hexane) to yield 6.5 mg of purple $\text{Os}_3(\text{CO})_{10}(\mu\text{-CNCF}_3)_2$ (**2**) (4%). Spectral data for **1**: IR (CH_2Cl_2) $\nu(\text{CO})$ 2121 (s), 2073 (m), 2059 (vs), 2037 (m), 1996 (w), $\nu(\text{CN})$ 1625 (m), 1588 (w) cm^{-1} ; ^{19}F NMR (in acetone- d_6 , 239 K, ref CFCl_3) $\delta -59.71$ (s, 3 F), -59.95 (s, 3 F). Anal. Calcd (found) for $\text{Os}_3\text{C}_{15}\text{F}_9\text{N}_2\text{O}_{11}$: C, 16.86 (16.85); N, 2.62 (3.26). Spectral data for **2**: IR (hexane) $\nu(\text{CO})$ 2123 (w), 2079 (vs), 2059 (s), 2033 (s), 2006 (m), $\nu(\text{CN})$ 1718 (w), 1696 (vw), 1661 (m) cm^{-1} ; ^{19}F NMR (in acetone- d_6 , 297 K, ref CFCl_3) $\delta -59.28$ (s, 6 F). Anal. Calcd (found) for $\text{Os}_3\text{C}_{14}\text{F}_8\text{N}_2\text{O}_{10}$: C, 16.16 (15.93); N, 2.69 (2.87). Crystals of both complexes suitable for X-ray diffraction studies were obtained from solutions in mixtures of dichloromethane/hexane by cooling to 4 °C.

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(6) Crystal data for **1**: space group $Pca2_1$; $a = 14.456$ (2) Å, $b = 11.077$ (2) Å, $c = 14.301$ (4) Å; $Z = 4$; 1714 reflections, $R = 0.029$. For **2**: space group $Pbcn$; $a = 26.940$ (6) Å, $b = 11.361$ (3) Å, $c = 14.450$ (2) Å; $Z = 8$; 1644 reflections, $R = 0.034$.

(7) Diffraction measurements at 20 °C were made on a Rigaku AFC6S four-circle diffractometer using Mo $K\alpha$ radiation. The structure solution and refinement were made by using the TEXSAN structure solving program library (v5.0) of the Molecular Structure Corp., The Woodlands, TX. An absorption correction was applied to the data.

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(9) A benzene (15 mL) solution of $\text{Os}_3(\text{CO})_{11}(\mu\text{-CNCF}_3)_2$ (**1**) (36 mg, 0.0337 mmol) was heated to reflux for 5 min. After the mixture was cooled to room temperature, the solvent was evaporated to dryness under nitrogen, and the residue was chromatographed by TLC on silica gel with a mixture of dichloromethane/hexane (1:4) to yield 30.4 mg of $\text{Os}_3(\text{CO})_{10}(\mu\text{-CNCF}_3)_2$ (87%).

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