

is attributed to both the large steric strains among the three linked six-membered rings and the low basicity of the ligand.

At pH values lower than 1.0, both the direct protonation pathway and the proton-assisted pathway make contributions to the rate. The ratio k_{2H}/k_{1d} represents the relative rate of dissociation at high acid concentration by the direct protonation and the proton-assisted pathways. As pointed out by Read and Margerum,¹⁰ if the donor is unrestricted and able to move easily out of the first coordination sphere, the presence of acid has little effect. However, if the movement of the donor away from the metal ion is hindered in some way, acid can enhance the rate of dissociation. The restrictions to hold the donor in the first coordination sphere imposed by the 6,5,6-membered chelate rings are larger than those imposed by the 6,6,6-membered chelate rings. Consequently, ring opening is easier for the 6,6,6-membered rings, making the direct protonation pathway less important. The results tabulated in Table II substantiate this point of view.

The acid dissociation reaction of $\text{Ni}(\text{en})^{2+}$ has been studied by Read and Margerum.¹⁰ This reaction is catalyzed by specific and general acids. In contrast with the behavior of $\text{Ni}(\text{en})^{2+}$, the results tabulated in Table I indicate that the rates of the dissociation reactions of these nickel(II) diamino diamide complexes do not depend on the concentrations of acetic, chloroacetic, and dichloroacetic acids. As shown in Figure 3, the rate-determining steps for both the direct protonation pathway ($\text{V} \rightarrow \text{VI}$) and the proton-assisted pathway at low pH ($\text{II} \rightarrow \text{III}$) do not involve a transfer of hydrogen ion from a Brønsted acid to the nickel(II) diamino diamide complex.

The values of k_{1d} and k_{2H} for the reactions of these nickel(II) diamino diamide complexes are smaller than those for the reactions of the corresponding copper(II) complexes; however, the values of k_d for the reactions of these nickel(II) diamino diamide complexes are larger than those for the reactions of the corresponding copper(II) diamino diamide complexes.¹ Of the transition-metal ions, copper(II) is one of the most kinetically labile. Each mechanistic rate constant for the reaction of the copper(II) complex is larger than that for the reaction of the corresponding nickel(II) complex; however, the value of $k_1 k_2 / k_{-1} k_{-2}$ for the reaction of the copper(II) complex is much smaller than that of the corresponding nickel(II) complex. In summation, k_d for the reaction of a copper(II) complex is smaller than that of the corresponding nickel(II) complex, consistent with a strong $\text{Cu}(\text{II})\text{-N}$ bond compared to the $\text{Ni}(\text{II})\text{-N}$ bond.

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Registry No. $\text{Ni}(\text{L-2,2,2})(\text{ClO}_4)_2$, 112816-41-8; $\text{Ni}(\text{5-Me-L-2,2,2})(\text{ClO}_4)_2$, 112816-45-2; $\text{Ni}(\text{L-2,3,2})(\text{ClO}_4)_2$, 112816-43-0; $\text{Ni}(\text{6-OH-L-2,3,2})(\text{ClO}_4)_2$, 112816-47-4; CH_3COOH , 64-19-7; CH_2ClCOOH , 79-11-8; CHCl_2COOH , 79-43-6.

Supplementary Material Available: Table I, giving part of the kinetic data for the dissociation of nickel(II) diamino diamide complexes in acid at 25.0 ± 0.1 °C and $\mu = 4.0$ M ($\text{NaClO}_4 + \text{HClO}_4$) (2 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of $\text{H}_3\text{Os}_3(\text{CO})_9(\mu_3\text{-CF})$. ^{13}C NMR Comparison of Triosmium- and Tricobalt-Substituted Methylidyne Complexes

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Alkylidynetriometal clusters have been synthesized and studied extensively in recent years,¹ in part since they may be related to

species occurring on metal surfaces during heterogeneous catalysis.² Though compounds of the formula $\text{M}_3(\mu_3\text{-CX})$ have been prepared for a variety of substituents X, the known examples for $\text{X} = \text{F}$ are limited to $\text{Co}_3(\text{CO})_9(\mu_3\text{-CF})$ ³ and certain of its carbonyl⁴ or metal-substituted⁵ derivatives together with $\text{Fe}_3(\text{CO})_9(\mu_3\text{-CF})_2$.⁶ Since ^{19}F is NMR active, the fluoromethylidyne ligand is a valuable probe for examining the electronic properties and bonding in $\text{M}_3(\mu_3\text{-CX})$ in clusters. We now report the synthesis and NMR characterization of the first fluoromethylidyne triosmium cluster together with a ^{13}C NMR comparison of analogous substituted methylidyne triosmium and tricobalt clusters.

Experimental Section

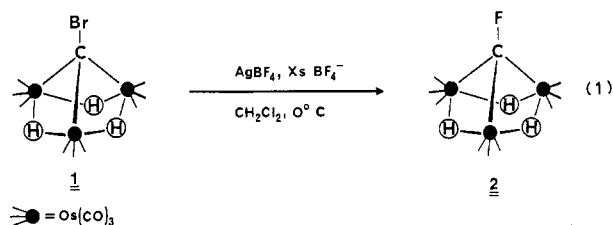
Reactions were conducted under a nitrogen atmosphere. Glassware was heated under vacuum prior to use in order to remove any moisture. Dichloromethane was freshly distilled from phosphorus pentoxide. AgBF_4 and $[\text{Et}_4\text{N}]\text{BF}_4$ were purchased from Aldrich Chemical Co. and used as received; both were handled in a N_2 -filled glovebox. Preparative TLC plates were prepared with E. Merck silica gel 60-GF 254. $\text{H}_3\text{Os}_3(\text{CO})_9(\mu_3\text{-CBr})$ (**1**) was prepared by a published procedure.⁷ A ^{13}C -enriched sample was prepared analogously, starting from ^{13}C -enriched $\text{Os}_3(\text{CO})_{12}$. ^1H and ^{19}F NMR spectra were obtained with a Varian EM-390 spectrometer. ^{13}C NMR spectra were obtained with a General Electric GN-500 NMR spectrometer at 125 MHz. Elemental analysis and mass spectra were obtained by the respective staffs of the Microanalytical Laboratory and of the Mass Spectrometry Laboratory in the School of Chemical Sciences.

Synthesis of $\text{H}_3\text{Os}_3(\text{CO})_9(\mu_3\text{-CF})$ (2**).** A solution of $\text{H}_3\text{Os}_3(\text{CO})_9(\mu_3\text{-CBr})$ (**1**) (23.5 mg, 0.026 mmol) and $[\text{Et}_4\text{N}]\text{BF}_4$ (150 mg, 0.69 mmol) in dry dichloromethane (30 mL) was degassed by evacuation and then placed under nitrogen. The flask was cooled in an ice bath, and then a solution of AgBF_4 (33.7 mg, 0.17 mmol) in dichloromethane (10 mL) was added via syringe. The solution color immediately turned yellow. The mixture was stirred for 50 min at 0 °C, during which time the solution color changed to dark yellow and then to light tan while a brown precipitate formed. The solution was filtered and separated by TLC. This provided white, solid **2** (13.8 mg, 63%). Two minor products observed on the TLC plate were not characterized.

Anal. Calcd for **2**: C, 14.02; H, 0.35; F, 2.22. Found: C, 13.95; H, 0.39; F, 2.10. ^1H NMR (CDCl_3): δ -18.80. ^{13}C NMR (CDCl_3): δ 212.45 ($\mu_3\text{-CF}$, $J(^{13}\text{C}, ^{19}\text{F}) = 370.9$ Hz), 165.9 (3 CO), 165.5 (6 CO). ^{19}F NMR (CDCl_3): -77.73 ppm (relative to external CFCl_3). IR (C_6H_{12}): $\nu(\text{CO})$ 2083 (vs), 2076 (w, sh), 2027 (vs), 2015 (m), 1986 (m) cm^{-1} . MS (EI, ^{192}Os): m/z 862 (M^+) and ($\text{M}^+ - x\text{CO}$, $x = 1-9$).

Results and Discussion

The reaction of **1** with AgBF_4 in dry dichloromethane in the presence of excess $[\text{NEt}_4]\text{BF}_4$ affords, after TLC purification, the fluoromethylidyne cluster **2** in 63% isolated yield (eq 1). The



formulation of **2** is established by microanalysis and mass spectrometry. The carbonyl IR spectrum is very similar to that of **1**, i.e., a typical pattern for such a symmetrical cluster.⁷ The ^1H NMR spectrum features a single hydride resonance at δ -18.80.

- (1) Review: Seyferth, D. *Adv. Organomet. Chem.* **1976**, *14*, 97.
- (2) Muettterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91.
- (3) Dent, W. T.; Duncanson, L. A.; Guy, R. G.; Reed, H. W. B.; Shaw, B. L. *Proc. Chem. Soc.* **1961**, 169.
- (4) (a) Penfold, B. R.; Robinson, B. H. *Acc. Chem. Res.* **1973**, *6*, 73. (b) Dawson, P. A.; Robinson, B. H.; Simpson, J. J. *Chem. Soc., Dalton Trans.* **1979**, 1762 and references therein.
- (5) (a) Beurich, H.; Vahrenkamp, H. *Chem. Ber.* **1982**, *115*, 2385. (b) Beurich, H.; Blumhofer, R.; Vahrenkamp, H. *Chem. Ber.* **1982**, *115*, 2409.
- (6) Lentz, S.; Bruedgam, I.; Hartl, H. *Angew. Chem.* **1985**, *97*, 115; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 119.
- (7) Keister, J. B.; Horling, T. L. *Inorg. Chem.* **1980**, *19*, 2304.

Table I. Comparative ^{13}C and ^{19}F NMR Data for Fluoromethylidyne Clusters

compd	$\delta(^{13}\text{C})$	$J(^{13}\text{C}, ^{19}\text{F}),^a$		ref
		Hz	$\delta(^{19}\text{F})$	
$\text{H}_3\text{Os}_3(\text{CO})_9(\mu_3\text{-CF})$	212.5	371	-77.7	this work
$\text{Co}_3(\text{CO})_9(\mu_3\text{-CF})$	309	498	+44.5 ^b	8, 9
$\text{Fe}_3(\text{CO})_9(\mu_3\text{-CF})_2$	365.8	452	+69.5	6

^a These coupling constants can be assumed to have a negative sign, see ref 11. ^b The authors of ref 8 used a reversed sign convention. The positive sign is in accord with the current convention that shifts downfield are positive.

The formation of **2** from **1** and AgBF_4 presumably occurs by bromine abstraction to generate the cation $[\text{H}_3\text{Os}_3(\text{CO})_9(\mu_3\text{-C})]^+$. If the observed intermediate yellow color can be attributed to the cluster carbocation, it must have a significant lifetime. Fluorine abstraction from the tetrafluoroborate counterion apparently produces the fluoromethylidyne product, since, in the absence of excess BF_4^- , only a low yield of **2** is obtained. Attempts to observe this putative intermediate directly are underway.

The ^{13}C and ^{19}F NMR data collected for **2** are given in Table I together with the analogous data available for the compounds $\text{Co}_3(\text{CO})_9(\mu_3\text{-CF})$ ^{8,9} and $\text{Fe}_3(\text{CO})_9(\mu_3\text{-CF})_2$.⁶ The ^{19}F NMR signal for **2** occurs at -77.7 ppm, a much more shielded position than that observed for the fluorine nucleus in either of the other fluoromethylidyne compounds. This is likely due in part to a heavy-atom effect, since the series of compounds $[\text{Co}_2(\text{CO})_6\text{-}\{\text{CpM}(\text{CO})_2\}(\mu_3\text{-CF})]$ shows a sequential upfield shift as $\text{M} = \text{Cr}$ (63.6 ppm) is replaced by Mo (38.4 ppm) and W (14.4 ppm).⁵ This effect obviates useful comparison with the resonances of fluorine nuclei bound to nonmetallic units (e.g., FCH_2CH_3 , -212 ppm; FCMe_3 , -132 ppm, FCCH , -95 ppm).¹⁰ The same effect apparently operates for ^{13}C NMR signals as well, since the fluoromethylidyne carbon in **2** resonates at significantly higher field than the corresponding carbons in either $\text{Fe}_3(\text{CO})_9(\mu_3\text{-CF})_2$ or $\text{Co}_3(\text{CO})_9(\mu_3\text{-CF})$ (vide infra). However, the carbon-fluorine coupling constant may be a better probe of the carbon environment, since it is significantly smaller in magnitude for **2** (371 Hz) than for either the tricobalt (498 Hz) or the triiron compound (452 Hz). Although coupling constants involving fluorine are not necessarily dominated by the Fermi-contact term,¹¹ the implication of a weaker C-F bond in **2** is consistent with our observation of $\nu(\text{CF})$ at 1067 cm^{-1} compared with that reported for $\text{Co}_3(\text{CO})_9(\mu_3\text{-CF})$ at 1164 cm^{-1} .^{4b}

Aime and co-workers have reported ^{13}C NMR chemical shift values for the substituted methylidyne carbon atoms in a series of compounds $\text{Co}_3(\text{CO})_9(\mu_3\text{-CX})$.⁹ Combining our current ^{13}C NMR data for **2** with previous data obtained in our group ($\text{X} = \text{H}$, δ 119.2; $\text{X} = \text{Cl}$, δ 145.4; $\text{X} = \text{Br}$, δ 124.1; $\text{X} = \text{C}_6\text{H}_5$, δ 153.7) provides an analogous set of chemical shifts for the compounds $\text{H}_3\text{Os}_3(\text{CO})_9(\mu_3\text{-CX})$. As shown in Figure 1, there is a reasonably linear correlation between the two sets of data. Most interestingly, however, the chemical shift range of the methylidyne carbon atom for various substituents X covers 46 ppm in the tricobalt case, whereas it is twice as big, 93 ppm, for the triosmium analogues. Thus, the apical carbon center in the triosmium complexes is much more sensitive toward substituents with varying bonding properties.

An explanation for this observation is suggested by work comparing $\text{Co}_3(\text{CO})_9(\mu_3\text{-CX})$ and $\text{H}_3\text{Ru}_3(\text{CO})_9(\mu_3\text{-CX})$ clusters in terms of photoelectron spectroscopy and MO calculations.¹² The apical carbon bonding in the tricobalt clusters is more delocalized, with extensive mixing of Co-Co and Co-C interactions, whereas the bridging hydrogens in the tri ruthenium clusters disrupt the metal-metal bonding and leave the Ru-C interactions more distinct. Extending these results to the congeneric triosmium

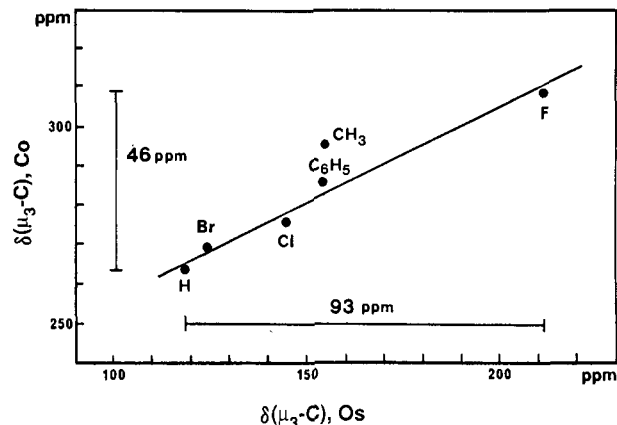


Figure 1. Comparison of the apical carbon ^{13}C NMR chemical shifts in $\text{H}_3\text{Os}_3(\text{CO})_9(\mu_3\text{-CX})$ and $\text{Co}_3(\text{CO})_9(\mu_3\text{-CX})$ ($\text{X} = \text{H}, \text{Cl}, \text{Br}, \text{C}_6\text{H}_5, \text{CH}_3, \text{F}$). The chemical shift for $\text{H}_3\text{Os}_3(\text{CO})_9(\mu_3\text{-CCH}_3)$ (154.7) was reported in ref 13.

complexes indicates that the methylidyne carbon in $\text{H}_3\text{Os}_3(\text{CO})_9(\mu_3\text{-CX})$ clusters will be more isolated electronically than that in $\text{Co}_3(\text{CO})_9(\mu_3\text{-CX})$ clusters and therefore less able to delocalize the electronic effects of changing the substituents. This variability in response complicates the issue of identifying characteristic chemical shifts for specific ligands in clusters for comparison with chemisorbed surface species.¹³

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Registry No. 1, 73746-96-0; 2, 112621-17-7.

(13) Evans, J.; McNulty, G. S. *J. Chem. Soc., Dalton Trans.* 1984, 79.

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Signs of Interphosphorus Nuclear Spin Coupling Constants in Octahedral Transition-Metal Complexes Containing Chelated Phosphine Ligands

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In a recent comment by Baker and Field¹ on internuclear spin-spin coupling in formally octahedral transition-metal phosphine complexes, it was claimed that the sign of $^2J(\text{PMP})$ for pairs of cis-related phosphorus atoms is generally negative and that this could be used as a basis for spectral assignments. We wish to point out that our own published and unpublished results²⁻⁶ demonstrate that this is not the case, particularly when chelating ligands are involved, as they are in the examples cited by Baker and Field.¹

It was proposed a decade ago by Grim et al.⁷ that the couplings formally described as $^2J(\text{PMP})$ in cis diphosphine chelate com-

(8) Beveridge, A. D.; Clark, H. C. *J. Organomet. Chem.* 1968, 11, 601.

(9) Aime, S.; Milone, L.; Valle, M. *Inorg. Chim. Acta* 1976, 18, 9.

(10) Dungan, C. H.; Van Wazer, J. R. *Compilation of Reported ^{19}F NMR Chemical Shifts*; Wiley: New York, 1970.

(11) Kalinowski, H.-O.; Berger, S.; Braun, S. *^{13}C -NMR-Spektroskopie*; Georg Thieme Verlag: Stuttgart, FRG, 1984, p 520 ff.

(12) Sherwood, D. E.; Hall, M. B. *Organometallics* 1982, 1, 1519.

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