was performed by using the program DIFABS.[34] The nitrosyl group appeared to occupy two general positions with a statistical occupancy of 0.5, and the corresponding N and O atoms [and also the C(3) atom] were refined with isotropic temperature factors, while the remaining non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at calculated positions and included in the structure factor calculations. Attempts to correct the data for secondary extinction gave no significant result. Refinement was on F with σ weights, $1/\sigma^2(F_o)$. The R and R_w values corresponding to the final cycle of full-matrix least-squares refinement are given in Table I.

Neutral-atom scattering factors were taken from Cromer and Waber;[35] those for tungsten were corrected for anomalous dispersion.[36] All calculations were performed with the Enraf-Nonius CAD4 SDP programs.[37]

(3) Electrochemistry. The solvent (benzonitrile) and the supporting electrolyte (Bu_4NPF_6) were purified as described earlier.[38] As some redox states of the compounds under study are very reactive toward oxygen, all of the experiments were conducted inside a nitrogen-atmosphere box, N_2 being purified continuously by passage through molecular sieves and BTS catalyst. As the presence of residual water affects the voltammograms of these compounds greatly, solutions of the supporting electrolyte (0.1 M Bu_4NPF_6) were prepared in the box, stored over molecular sieves (Linde 4A), and dried just before use by two successive percolations through activated (400 °C under vacuum for 48 h) neutral alumina (Merck) columns. From the observation of the effect of added water on the background current, the concentration of residual water in the electrolyte solution is estimated to be less than 0.05 mM.

Apparatus. A three-compartment microelectrochemical cell has been specially designed. The platinum (2 mm) or glassy-carbon (3 mm) rotating-disk electrode (EDI-Tacussel) is adapted to the main compartment through a ground joint (14.5/23). The auxiliary and reference electrodes are connected at the bottom of the cell via ground joints (7/16); they are terminated by Vycor tips (PAR). Such a cell allows cyclic and rotating-disk voltammetry to be performed on 0.3–0.5 mL of solution. The small volume of solution can be electrolyzed completely, directly in the same cell, by using the rotating-disk electrode.

The reference electrode used is the half-cell: Pt/ferrocenium picrate (10^{-2} M), ferrocene (10^{-2} M), Bu_4NPF_6 (0.2 M), benzonitrile. For comparison of the present results with other work, the Fc/Fc^+ formal potential has been measured versus SCE in benzonitrile (0.2 M Bu_4NPF_6): $E^{\circ\prime}(Fc/Fc^+) = +0.43$ V vs SCE.

A Model 173 potentiostat (PAR) monitored by a Model 175 programmer (PAR) and a T2-Y x-y chart recorder (Sefram-Enertec) were used for the electrochemical investigations.

Acknowledgment. We thank the DRET for financial support of this research.

Supplementary Material Available: Tables of general temperature factor expressions U's, bond distances and bond angles for the $C_{24}H_{27}N_5$ ligand, and least-squares planes (7 pages); a table of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization by ^1H, ^{13}C, and ^{19}F NMR Spectroscopy of $(CH_3CN)_n(CO)_{4-n}(NO)W(\mu\text{-}F)BF_3$ and $[(CH_3CN)_{n+1}(CO)_{4-n}(NO)W][BF_4]$ (n = 0–2), Tungsten Mononitrosyl Carbonyl Cations with Labile Acetonitrile and $[(\mu\text{-}F)BF_3]^-$ Ligands

William H. Hersh[†]

Received June 8, 1989

Addition of $[NO][BF_4]$ to $CH_3CNW(CO)_5$ in CH_2Cl_2 gives a mixture of five mononitrosyl compounds, *mer*-(*cis*-CH_3CN)(*trans*-NO)$(CO)_3W(\mu\text{-}F)BF_3$ (**1**), [*mer*,*cis*-$(CH_3CN)_2W(CO)_3(NO)][BF_4]$ (**2a**), *cis*,*cis*,*trans*-$(CH_3CN)_2(CO)_2(NO)W(\mu\text{-}F)BF_3$ (**3**), [*fac*-$(CH_3CN)_3W(CO)_2(NO)][BF_4]$ (**4a**), and *trans*-$(NO)(CO)_4W(\mu\text{-}F)BF_3$ (**5**); in a typical experiment the yield is 90%, and the ratio **1**:**2a**:**3**:**4a**:**5** is 47:14:11:1:27. Addition of acetonitrile to the mixture results in substitution of the $[(\mu\text{-}F)BF_3]^-$ ligand of **1**, **3**, and **5** with conversion to **2a**, **4a**, and [*trans*-$(CH_3CN)W(CO)_4NO][BF_4]$ (**6**), respectively; allowing the mixture to stand in the presence of excess acetonitrile results in complete conversion of **2a** and **6** to **4a**. Further support for the identities of **1**–**5** is obtained by reaction of the mixture with Me_3P, giving [*mer*-(*cis*-CH_3CN)(*trans*-$Me_3P)W(CO)_3(NO)][BF_4]$ (**7a**), [*cis*,*cis*,-*trans*-$(CH_3CN)_2(CO)_2(NO)W(PMe_3)][BF_4]$ (**8a**), [*trans*-$Me_3P(CO)_4WNO][BF_4]$ (**9**), and the previously reported compound [*mer*,*cis*-$(Me_3P)_2W(CO)_3(NO)][BF_4]$ (**10a**). The reaction mixtures are analyzed by IR and ^1H, ^{13}C, and ^{19}F NMR spectroscopy. In particular, the ^{13}C NMR spectrum exhibits quintets for the carbonyl ligands of **1**, **3**, and **5** due to a dynamic "spinning" process of the $[(\mu\text{-}F)BF_3]^-$ ligand, and the ^{19}F NMR spectrum exhibits doublets for the terminal fluorine atoms (which are further separated into ^{10}B and ^{11}B isotopomers) near −153 ppm and quartets for the bridging fluorine atoms from −203 to −238 ppm. Independent synthesis and isolation in good yield of **2b**–**c**, **4a**–**d**, **7b**–**c**, and **8b** (where the anions for **a**–**d** are $[BF_4]^-$, $[SbF_6]^-$, $[(C_6H_5)_4B]^-$, and $[PF_6]^-$, respectively) are described, as are the independent synthesis and spectroscopic characterization of **3**, **5**, and **6**.

Introduction

Mononuclear tungsten carbonyl complexes have been studied intensively over the years, in part due to their relatively high thermal stability.[1] The octahedral d^6 complexes are both coordinatively and electronically saturated and so for instance serve as ideal templates for stabilizing reactive organic fragments such as carbenes and carbynes.[2] This high stability makes such complexes unlikely candidates for catalysis, however, and with the exception of the olefin metathesis reaction—where the ligand sphere of the tungsten carbonyl catalyst *precursor* may be quite different from the ligand sphere of the *catalyst*[3] that forms in the

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(1) (a) Angelici, R. J. *Organomet. Chem. Rev.* **1968**, *3*, 173–226. (b) Dobson, G. R. *Acc. Chem. Res.* **1976**, *9*, 300–306.
(2) See for instance: (a) Fischer, E. O. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic Press: New York, 1976; Vol. 14, pp 1–32. (b) Casey, C. P.; Burkhardt, T. J.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2127–2134. (c) Birdwhistell, K. R.; Tonker, T. L.; Templeton, J. L. *Ibid.* **1985**, *107*, 4474–4483. (d) McDermott, G. A.; Dorries, A. M.; Mayr, A. *Organometallics* **1987**, *6*, 925–931.

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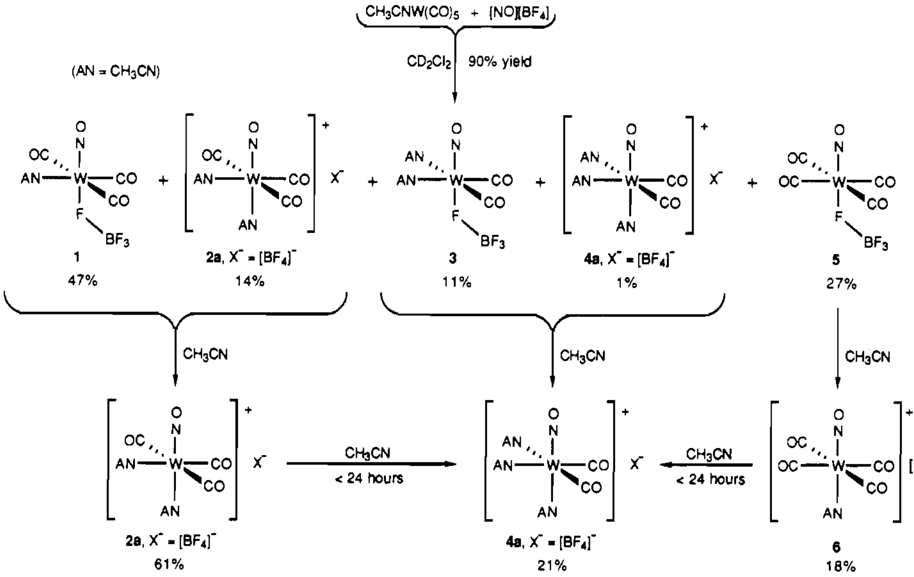
Scheme I



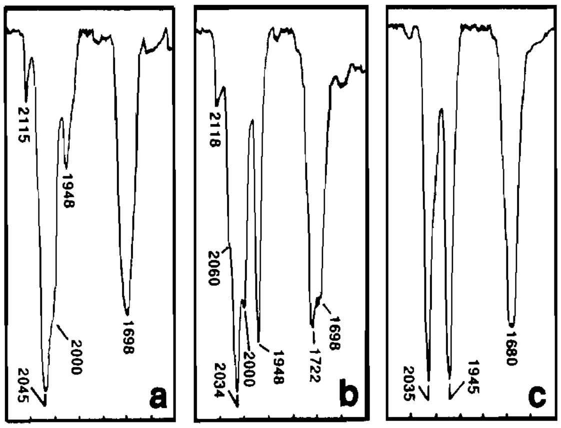
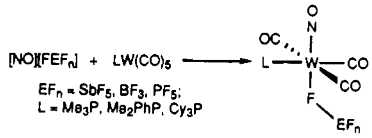


Figure 1. Infrared spectra from 2200 to 1500 cm^{-1} of the reaction of $CH_3CNW(CO)_5$ with $[NO][BF_4]$ in CH_2Cl_2 recorded (a) after cessation of CO evolution, (b) immediately after addition of 2 equiv of CH_3CN to the reaction mixture in (a), and (c) 4 h after addition of 2 equiv of CH_3CN to the reaction mixture in (a).

presence of the required Lewis acid cocatalyst[4]—examples are rare. These include Trost's work on allylic alkylation catalyzed by $(AN)_3W(CO)_3$ (AN = CH_3CN),[5] Sen's work on dinitrosyl dications, in which $[(AN)_4M(NO)_2]^{2+}$ (M = Mo, W) was found to be an active olefin rearrangement, oligomerization, and polymerization catalyst,[6] and Legzdins's discovery that $CpW(NO)_2(\mu\text{-}F)BF_3$ (Cp = $\eta^5\text{-}C_5H_5$) is also an olefin isomerization and dimerization catalyst.[7] The first two compounds incorporate labile acetonitrile ligands, while in the latter two the cationic nitrosyl ligand has been used in place of the isoelectronic but neutral carbonyl ligand, in order to give catalytically active materials. The combination of acetonitrile and nitrosyl ligands in $[(AN)_4W(NO)_2]^{2+}$ results from the strong π-acidity of the nitrosyl ligand; carbonyl ligands rarely remain on the tungsten atom in dinitrosyl complexes.[8]

The goal of the work to be reported here is the high-yield synthesis of mononitrosyl tungsten cations, with the expectation that the resultant attenuation of π-acidity due to the presence of only a single nitrosyl ligand will allow carbonyl ligands to remain bound to the tungsten atom. Such compounds would provide a bridge between the stable but relatively unreactive neutral tungsten carbonyl complexes and the electrophilic and highly reactive carbonyl-free tungsten dinitrosyl dications. We recently described the nitrosylation of (alkylphosphine)pentacarbonyltungsten complexes as shown in eq 1,[9] in which mononitrosyl compounds were



$$[NO][FEF_n] + LW(CO)_5 \longrightarrow L(OC)_3W(NO)(F\text{-}EF_n) \qquad (1)$$

isolated in high yield as yellow crystalline solids, with each of the labile $[SbF_6]^-$, $[BF_4]^-$, and $[PF_6]^-$ ligands bound to tungsten via a fluorine bridge. This report presents synthetic results on the nitrosylation of $CH_3CNW(CO)_5$, in which the strong σ-donor phosphine ligand of the compounds in eq 1 has been replaced by the weaker donor acetonitrile ligand.

Results

Infrared Spectra. Nitrosylation of $(AN)W(CO)_5$ (AN = CH_3CN) in methylene chloride was carried out by reaction with $[NO][BF_4]$. The yellow suspension evolved carbon monoxide vigorously for several minutes as the nitrosonium salt dissolved, giving a yellow to greenish yellow solution. Interpretation of the observed results will be simplified by referring to the proposed structures **1–6** (Scheme I) of the new compounds to be described. The infrared spectrum of this initial reaction mixture consisted of bands due to a number of terminal carbonyl ligands (2115 (w), 2045 (s), 2000 (m, shoulder), 1948 (m) cm^{-1}) and a strong broad nitrosyl band at 1698 cm^{-1} (Figure 1a); the absence of the very strong broad band at 1930 cm^{-1} due to $(AN)W(CO)_5$ showed that

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(3) (a) Basset, J. M.; Bilhou, J. L.; Mutin, R.; Theolier, A. *J. Am.Chem. Soc.* **1975**, *97*, 7376–7377. (b) Bilhou, J. L.; Basset, J. M.; Mutin, R.; Graydon, W. F. *Ibid.* **1977**, *99*, 4083–4090. (c) Leconte, M.; Basset, J. M. *Ibid.* **1979**, *101*, 7296–7302.

(4) For metathesis and related examples using tungsten carbonyl compounds in the absence of Lewis acids, see: (a) Katz, T. J. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic Press: New York, 1977; Vol. 16, pp 283–317. (b) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422–424. (c) Katz, T. J.; Lee, S. J.; Nair, M.; Savage, E. B. *Ibid.* **1980**, *102*, 7942–7944.

(5) (a) Trost, B. M.; Hung, M.-H. *J. Am. Chem. Soc.* **1983**, *105*, 7757–7759. (b) Trost, B. M.; Hung, M.-H. *Ibid.* **1984**, *106*, 6837–6839. (c) Trost, B. M.; Tometzki, G. B.; Hung, M.-H. *Ibid.* **1987**, *109*, 2176–2177. For examples using $Mo(CO)_6$, see: (d) Trost, B. M.; Lautens, M. *Ibid.* **1987**, *109*, 1469–1478.

(6) (a) Sen, A.; Thomas, R. R. *Organometallics* **1982**, *1*, 1251–1254. (b) Sen, A. *Acc. Chem. Res.* **1988**, *21*, 421–428.

(7) Legzdins, P.; Martin, D. T. *Organometallics* **1983**, *2*, 1785–1791.

(8) (a) Green, M.; Taylor, S. H. *J. Chem. Soc., Dalton Trans.* **1972**, 2629–2631. (b) Kolthammer, B. W. S.; Legzdins, P.; Malito, J. T. *Inorg. Chem.* **1977**, *16*, 3173–3178. For more typical examples (where all the carbonyl ligands are lost) see ref 6 and the following: (c) Clamp, S.; Connelly, N. G.; Taylor, G. E.; Louttit, T. S. *J. Chem. Soc., Dalton Trans.* **1980**, 2162–2169. (d) Legzdins, P.; Oxley, J. C. *Inorg. Chem.* **1984**, *23*, 1053–1059.

(9) (a) Hersh, W. H. *J. Am. Chem. Soc.* **1985**, *107*, 4599–4601. (b) Honeychuck, R. V.; Hersh, W. H. *Inorg. Chem.* **1989**, *28*, 2869–2886.

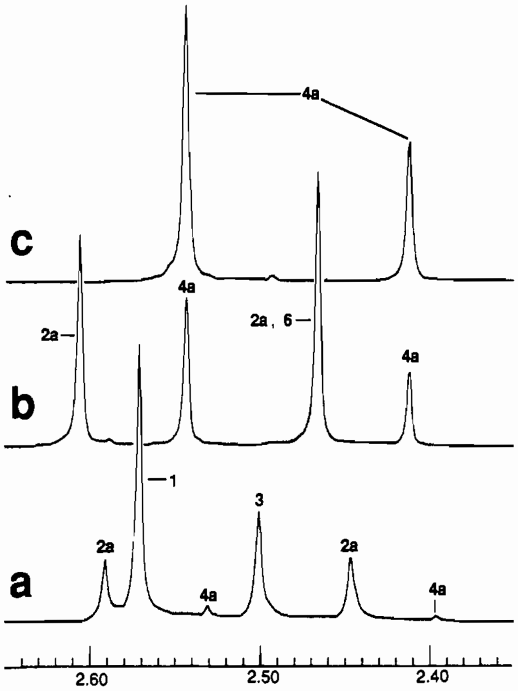

Figure 2. ^1H NMR spectra (200 MHz; CH_3CN region only) of the reaction of $CH_3CNW(CO)_5$ with $[NO][BF_4]$ in CD_2Cl_2 recorded (a) after cessation of CO evolution, (b) after addition of 2 equiv of CH_3CN to the reaction mixture in (a), and (c) 24 h after addition of 2 equiv of CH_3CN to the reaction mixture in (a).

consumption of the starting material was complete. The key bands are those at 2115 and 1698 cm^{-1}, the former indicative of a pair of *trans*-carbonyl ligands on a tungsten nitrosyl center, and the latter indicative of *mono*nitrosyl compounds rather than dinitrosyl dications.[6,8a] Since the major component of the reaction mixture was **1** (vide infra), the bands at 2115, 2045, 2000, and 1698 cm^{-1} reasonably can be assigned to it. Addition of 2 equiv of acetonitrile (Figure 1b) resulted in apparent complication of the infrared spectrum by splitting the bands at 2045 and 1698 cm^{-1}. The major component was **2a** (2118, 2060, 2034, 2000, 1722 cm^{-1}) formed by displacement of the labile $[BF_4]^-$ ligand (vide infra), while the minor component was **4a** (2034, 1948, ~1698 cm^{-1}). It is interesting to note that the acetonitrile ligand trans to the nitrosyl ligand gives a ***higher*** nitrosyl stretching frequency in **2a** than does the weaker donor $[BF_4]^-$ in **1**; while in contrast to expectation, we have observed and discussed this phenomenon in related systems.[9b] Allowing the reaction mixture to stand for 4 h at room temperature gave a clear orange solution that exhibited three strong bands in the infrared spectrum (Figure 1c) at 2035, 1945, and 1680 cm^{-1}, due to conversion of **2a** into **4a** by substitution of CO with acetonitrile. After 4 h in the *absence* of the additional acetonitrile, the initial reaction mixture was somewhat more orange (due to **4a**) and some brown precipitate had formed, but little change was observed in the infrared spectrum apart from a small increase in the intensity of the band at 1948 cm^{-1} due to **4a**.

Quantitative ^1H NMR Experiments. Examination of the ^1H NMR spectrum (Figure 2a) not only confirmed but also increased the complexity suggested by the infrared spectra. The reaction was carried out in a similar manner, but in CD_2Cl_2, and after filtration of the solution 1,2-dichloroethane was added as an internal integration standard. Six acetonitrile methyl singlets were seen due to **1**, **2a**, **3**, and **4a** in relative ratios of 64:19:15:2 (Scheme I). These percentages are fairly reproducible, although allowing the reaction mixture to stand or removing the solvent followed by redissolving in fresh methylene chloride gave rise to sufficient variability in the relative peak heights to assign the signals to *five* independent sets (vide infra). The most surprising result of this experiment is that while the yield of products **1**–**4** (determined with respect to the internal standard) based on acetonitrile was 90%, *the yield based on tungsten was only 66%*. That is, one-third of the tungsten initially present as $(AN)W(CO)_5$ could not be accounted for, and since no significant amount of insoluble material was formed in the reaction and no $W(CO)_6$ was detected by infrared spectroscopy (at 1970 cm^{-1}), a ^1H NMR-silent tungsten compound presumably was present.

As with the infrared spectrum, addition of excess acetonitrile (2.4 equiv) immediately converted **1** to **2a** and **3** to **4a** (Scheme I); a slight downfield shift for the acetonitrile signals was also observed in the ^1H NMR spectrum as can be seen in Figure 2b, but while the change is likely due to the concentration increases of **2a** and **4a** that will alter the degree of ion pairing and hence the chemical shifts (vide infra), this issue has not been pursued. Close inspection of this spectrum showed that the height (and integral) of the high-field signal of **2a** at δ 2.47 was greater than that of the low-field signal at δ 2.61. This observation is completely reproducible and led to the hypothesis that an acetonitrile-free nitrosylation product undergoes substitution of coordinated $[BF_4]^-$ by acetonitrile to give a new compound having an acetonitrile peak overlapping with that of **2a** at δ 2.47. The proposal that these compounds are **5** and **6** was then used in a quantitative evaluation of the yields of **1**–**6**. That is, the assumption that **6** is a *mono*-acetonitrile adduct allows the yield of **6** to be computed as 16.5 ± 2.3% (based-on tungsten), so the total yield of *tungsten*-containing compounds **2a**, **4a**, and **6** after acetonitrile addition is 90 ± 5%, in remarkable agreement with the initially measured yield *prior* to acetonitrile addition of 90 ± 1% *based on acetonitrile*. Thus, both yield measurements leave 10% of the initial tungsten starting material unaccounted for. Since the initial yield of **1**–**4** based on tungsten was 66%, it is reasonable to compute the yield of **5** as the difference, namely, 24%, so that nitrosylation of $(AN)W(CO)_5$ actually gave **1**–**5** in the relative ratios of 47:14:11:1:27. Addition of acetonitrile to the mixture then gave **2a**, **4a**, and **6** in relative ratios of 61:21:18. While a more conservative estimate might equate the yield of **5** with the 16.5% yield of **6**, the smaller yield of **6** is in fact consistent with conversion to **2a** and **4a** prior to recording the NMR spectrum, as will be seen below. Since the total yields before and after acetonitrile addition were both 90%, for convenience only the relative ratios will be referred to in the following discussion. Thus, conversion of **1** to **2a** was quantitative, since the combined *mer*-adducts **1** and **2a** from $(AN)W(CO)_5$, and **2a** following acetonitrile addition to the mixture, identically made up 61% of the mixture, while the amount of **4a** following acetonitrile addition (21% of the mixture) was ***higher*** than the combined 12% of *fac*-adducts **3** (compounds derived from **4a** by substitution trans to NO will be designated as facial in this discussion) and **4a** from $(AN)W(CO)_5$, requiring that substitution of $[BF_4]^-$ from **3** not be the sole source of **4a**. While **5** is one obvious source of the additional **4a**, since it decreases from the calculated 27% of the mixture to 18% of the mixture (as **6**) following addition of acetonitrile, allowing the reaction mixture to stand for 24 h in the presence of excess acetonitrile resulted in complete conversion of *both* **2a** and **6** to **4a** (Figure 2c; Scheme I). That is, addition of acetonitrile to **5** is evidently (as will be confirmed below) the *ultimate* source of the additional **4a** as well as of **6**, but since **6** apparently also yields **2a**, the amount of **2a** converted to **4a** must have fortuitously been the same as the amount of **6** converted to **2a** in this experiment. The final yield of **4a** based on tungsten was 95 ± 3%, again in reasonable agreement with the yields made on the basis of the assumed structures of **5** and **6**.

In order to corroborate the above scheme, a similar pair of experiments were carried out by using trimethylphosphine instead of acetonitrile (Scheme II). In the first, ~0.8 equiv of Me_3P was added to an initial reaction mixture containing **1**–**5** in a ratio of 52:19:11:2:16 (where the amount of **5** was estimated from the amount of **6** formed upon acetonitrile addition). Surprisingly, $[BF_4]^-$ adducts **1** and **3** were still present, suggesting that the strongly nucleophilic Me_3P ligand[10] is relatively nonselective in displacing acetonitrile and $[BF_4]^-$. Two new compounds were identified, the major *mer*-adduct **7a** and the minor *fac*-adduct **8a**. The *mer*-adducts **1**, **2a**, and **7a** made up 77% of the mixture

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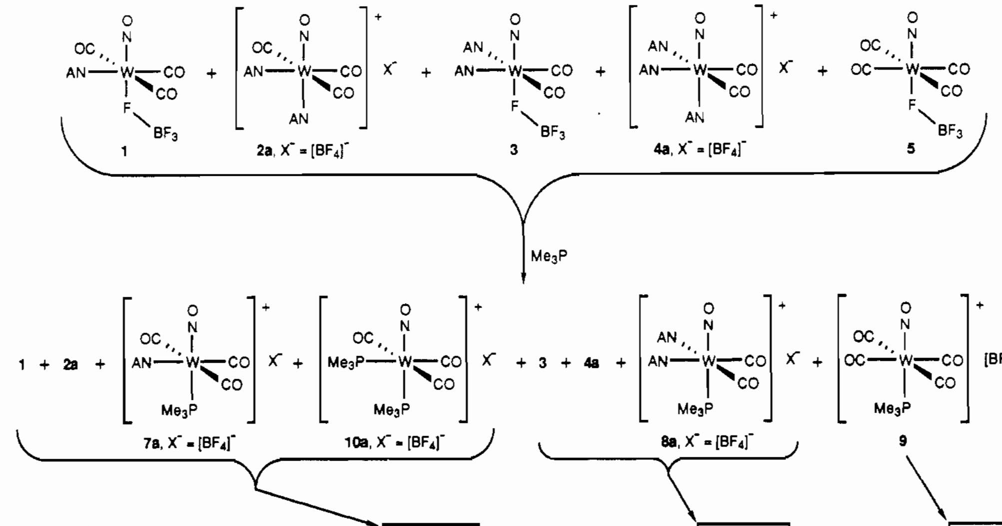
(10) Honeychuck, R. V.; Hersh, W. H. *Inorg. Chem.* **1987**, *26*, 1826–1828.

Scheme II



equivalents Me_3P	1	2a	7a	10a	Total *mer*-adducts	3	4a	8a	Total *fac*-adducts	5	9	Total *trans*-adducts
0	52%	19%	-	-	71%	11%	2%	-	13%	16%	-	16%
0.8	2%	16%	59%	0%	77%	2%	4%	6%	13%	-	11%	11%
2	0%	0%	35%	42%	78%	0%	0%	11%	11%	-	11%	11%

compared to 71% for **1** and **2a** in the initial mixture, while the *fac*-adducts **3**, **4a**, and **8a** made up 13% compared to 13% for **3** and **4a** in the initial mixture; the slight increase in **4a** was presumably due to release of acetonitrile from **2a** upon conversion to **7a**. A compound having only a phosphine doublet at δ 1.785 ($^2J_{PH}$ = 9.9 Hz) accounted for the remaining 11% of the mixture, assuming that it is a monophosphine compound, and it is presumed to be [*trans*-$Me_3P(CO)_4WNO$][BF_4] (**9**) derived from **5**; while **5** was not quantified in this experiment, the constant amount of **9** formed (vide infra) suggests that, unlike **1** and **3**, all of the **5** was consumed by Me_3P. We have obtained an X-ray structure on the analogous $[SbF_6]^-$ salt that precipitates following apparent cis–trans isomerization of the carbonylation product of *mer*-(*cis*-Me_3P)(*trans*-NO)$(CO)_3W(\mu$-F)SbF_5, and while preliminary evidence suggests that the trans isomer exhibits a doublet at δ 1.78 ($^2J_{PH}$ = 9.3 Hz) with the unrearranged cis isomer at δ 1.96 ($^2J_{PH}$ = 9.7 Hz), the compound is too insoluble to permit definitive assignment of the structures in solution in present.[11] Addition of ~2 equiv of Me_3P to the original nitrosylation mixture led to complete consumption of the adducts with $[BF_4]^-$ or acetonitrile trans to the nitrosyl ligand, giving *mer*-adducts **7a** and **10a**—where disubstitution of acetonitrile has occurred—(78% of the mixture), *fac*-adduct **8a** (11% of the mixture), and putative **9** (11% of the mixture). The two phosphine experiments support the proposed identities of **1**, **3**, and **5**, in that the *mer* and *fac* compositions of the initial nitrosylation mixture and the two phosphine substitution mixtures are comparable, as are the proposed relative amounts of trans-adducts **5** and **9**.

^{13}C NMR Spectrum. While **5** is not visible in the ^{1}H NMR spectrum, it was readily observed and identified by ^{13}C NMR spectroscopy. The key feature is that it along with **1** and **3** would be expected to be immediately identifiable as a [(μ-F)BF_3]$^-$ adduct by the observation of *quintets* for each carbonyl carbon due to C–F coupling, by comparison to the ^{13}C NMR spectra of *mer*-(*cis*-Me_3P)(*trans*-NO)$(CO)_3W(\mu$-F)EF_n (EF_n = BF_3 (**11a**), SbF_5 (**11b**)).[9b] The dynamic anion "spinning" process that generates the quintets in **11a**, for instance, has been described in detail and is ascribed to a process in which W–(μ-F) bond cleavage gives a tight ion pair followed by ion pair recombination—that is, "internal return"—so that each of the four fluorine atoms exchanges into the bridging site; $^2J_{CF}$ (of 9–11 Hz in the Me_3P adducts) is given by the distance between the two *outermost* lines of the quintet.[12] The nitrosylation sample was prepared in situ in CD_2Cl_2 as described above, and it gave a spectrum at 265 K (Figure 3) in which the major features (see Experimental Section for details) consisted of four carbonyl peaks that exhibited coupling to fluorine due to **1**, **3**, and **5** and two sharp singlets due to the carbonyl ligands of **2a**, as well as peaks for the acetonitrile ligands of **1–3**. The major carbonyl bands were two quintets at 206.1 ppm ($^2J_{CW}$ = 8 Hz) and 197.4 ppm ($^2J_{CW}$ = 11 Hz) in a 1:2 ratio due to the carbonyl ligands trans and cis, respectively, to the

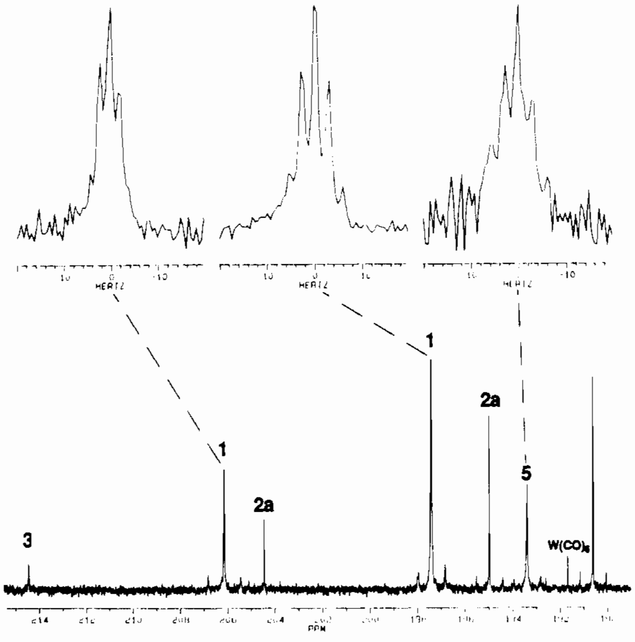


Figure 3. ^{13}C NMR spectrum (125.8 MHz; CO region only) of the reaction of $CH_3CNW(CO)_5$ with [NO][BF_4] in CD_2Cl_2. The full spectrum displayed was acquired at 265 K and processed by using exponential multiplication to reduce noise and allow the ^{183}W satellites to be observed (on all peaks except those due to **3** near 214 ppm and $W(CO)_6$ near 192 ppm). The expanded peaks are all plotted on the same scale and were processed with Gaussian multiplication to better show their quintet structure; for **1** (206 and 197 ppm) the 265 K spectrum is shown, while for **5** the 208 K spectrum is shown. The singlet (with ^{183}W satellites) at 190.6 ppm was not identified (see Experimental Section).

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(11) Honeychuck, R. V. Unpublished results. See also ref 10.

(12) Honeychuck, R. V.; Hersh, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 6056–6070.

Table I. Rate Constants[a] and Activation Parameters[a] Measured by ^{13}C NMR Spectroscopy for Intra- and Intermolecular $[BF_4]^-$ Exchange in **1** and **5**

	1		**5**	
	206 ppm	197 ppm	193 ppm	**11a**[b]
k_{intra}(208 K)	150 ± 50	200 ± 25	(250 ± 50)	470[c]
k_{intra}(265 K)	275 ± 25	325 ± 25[d]		4000[c]
k_{inter}(208 K)			4 ± 1	0.06[c]
k_{inter}(265 K)	(2.0 ± 0.5)	3.0 ± 0.5[d]	9 ± 1	2.2[c]
$\Delta G^{\ddagger}_{intra}$(208 K)	9.9[e]		(9.7)	9.5 ± 0.6[f]
$\Delta G^{\ddagger}_{intra}$(265 K)	12.4[e]			9.9 ± 0.7[f]
$\Delta G^{\ddagger}_{inter}$(208 K)			11.5[g]	13.2 ± 0.3[h]
$\Delta G^{\ddagger}_{inter}$(265 K)	(15.0)		14.3[g]	15.0 ± 0.4[h]

[a] Rate constants in s^{-1}, $\Delta G^{\ddagger}$ in kcal/mol; values in parentheses are for cases where the fit of the theoretical to observed line shape is relatively poor. [b] *mer*-(*cis*-Me_3P)(NO)$(CO)_3W(\mu\text{-}F)BF_3$. [c] Extrapolated or interpolated rate constant from data measured by ^{31}P NMR spectroscopy.[12] [d] Fit of the theoretical to observed line shape is imperfect for both intra- and intermolecular exchange; see text. [e] $\Delta H^{\ddagger}_{intra}$ = 0.6 kcal/mol, $\Delta S^{\ddagger}_{intra}$ = −45 eu. [f] $\Delta H^{\ddagger}_{intra}$ = 8.1 ± 0.4 kcal/mol, $\Delta S^{\ddagger}_{intra}$ = −7 ± 2 eu. [g] $\Delta H^{\ddagger}_{inter}$ = 1.1 kcal/mol, $\Delta S^{\ddagger}_{inter}$ = −50 eu. [h] $\Delta H^{\ddagger}_{inter}$ = 6.4 ± 0.3 kcal/mol, $\Delta S^{\ddagger}_{inter}$ = −33 ± 1 eu.

acetonitrile ligand in **1**. A weak signal assigned to the carbonyl ligands of **3** was observed at 214.5 ppm; while it was not a fully resolved quintet, the estimated coupling constant of 8 Hz is in agreement with that seen for the carbonyl ligand trans to acetonitrile in **1**, as might be expected. Further support for this assignment is obtained by comparison to the chemical shifts of independently prepared **2b** and **4b** (vide infra; X^- in Scheme I is $[SbF_6]^-$), where the carbonyl band of **4b** at 213.0 ppm is 1.5 ppm upfield of that in **3**, while the *trans*-carbonyls of **2b** at 195.0 ppm and the unique carbonyl at 204.2 ppm are also ~2 ppm upfield of those in **1**. Thus, substitution of the $[(\mu\text{-}F)BF_3]^-$ ligand for the trans-acetonitrile ligand of **2** and **4** has little effect on the carbonyl chemical shifts. The remaining fluorine-coupled peak appeared as a broad band at 193.4 ppm, with tungsten satellites giving $^1J_{CW}$ = 141 Hz, and is assigned to **5**. Support for this assignment, like that above for **1** and **3**, comes from chemical shift and coupling constant comparisons, in this case with *trans*-$BrW(CO)_4NO$ (190.26 ppm, $^1J_{CW}$ = 134 Hz), which is related to **5** by formal substitution of the $[(\mu\text{-}F)BF_3]^-$ ligand by Br^-. The relative amounts of **1**, **2a**, **3**, and **5** were determined by integration of the carbonyl bands; **5** made up 17 mol % of the mixture, while the ratio **1**:**2a**:**3** was 82:11:7. Since the amounts of **5** as estimated from the ^1H NMR spectra above ranged from 16–24% of the samples, and the ratio **1**:**2a**:**3** observed by ^1H NMR spectroscopy following the ^{13}C NMR spectrum was 75:18:7, these two types of spectra provide good support for the assignments, even if the ^{13}C integrations are considered approximate.

The ^{13}C NMR spectrum of **1**, **2a**, **3**, and **5** was also run at 208 K in an attempt to freeze out the intramolecular anion-spinning process. For **1** and **3**, only broadening of the quintets occurred by this temperature rather than sharpening to doublets, while for **5** the signal that was broad at 265 K was significantly sharpened into a clear *quintet* rather than a doublet at 208 K. This latter result means that the observed broadening in the high-temperature NMR spectrum of **5** is due to *inter*molecular exchange due to dissociation to free ions. Results of a line shape analysis are given in Table I, where rate constants for both the intramolecular spinning process and the intermolecular dissociation were determined as described previously for **11a**.[12] For **1**, the best fits of theoretical to observed line shapes were found for the intramolecular process, although the band at 197 ppm at 265 K might have been better fit to a combination of the two mechanisms. For **5**, the intramolecular exchange mechanism gave a poor fit at 208 K, so it is likely that only the intermolecular exchange is visible. That is, unlike the case described previously for **11a** where the inter- and intramolecular exchange regimes are both accessible and well separated, it appears that for **1** the two regimes overlap at 265 K, while for **5** intermolecular exchange is sufficiently rapid even at 208 K to mask any effects due to intramolecular exchange. The overlap in rate regimes for **1** means that some of the broadening at 265 K is due to *inter*molecular exchange rather than a relatively slow rate of spinning, so the rate constant of ~300 s^{-1} is probably badly underestimated, especially given the order of magnitude greater rate constant for **11a**. Similarly for **5**, if the spinning at 208 K is not at the fast-exchange limit, some of the broadening ascribed to *inter*molecular dissociation could be due to *intra*molecular spinning, so the rate constant could in this case be overestimated. The unfortunate consequence is that for both **1** and **5**, comparisons of intra- and intermolecular rate constants at the same temperature cannot be made with any confidence, even though for **1** $\Delta G^{\ddagger}_{intra}$(208 K) = 9.9 kcal/mol and for **5** $\Delta G^{\ddagger}_{inter}$(265 K) = 14.3 kcal/mol may be accurate. Study of the phosphine adduct **11a** was rendered convenient by the 5 kcal/mol difference in activation energy for the intra- and intermolecular processes at 265 K, but presumably the difference for **1** and **5** is less; further study of the anion exchange here has not been attempted.

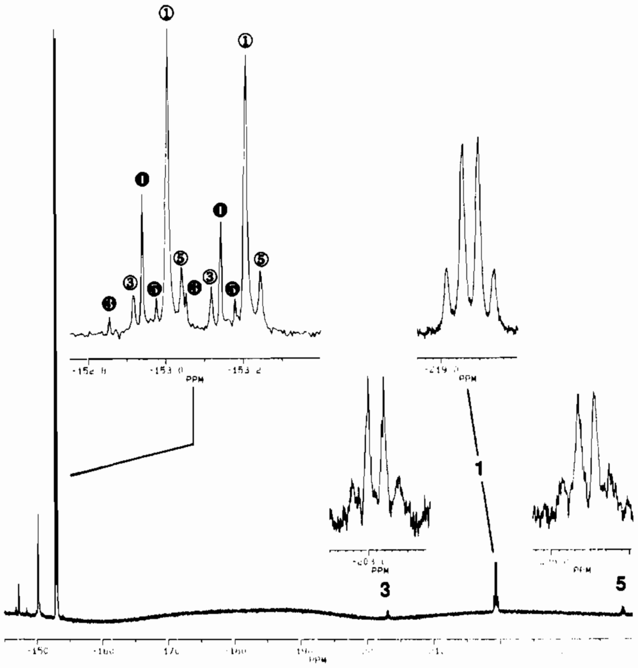
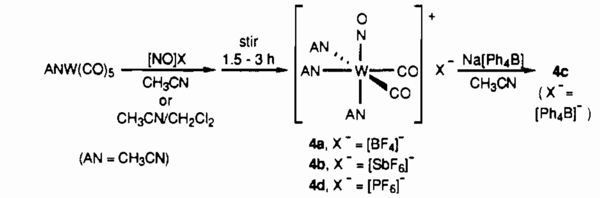


Figure 4. ^{19}F NMR spectrum (470.6 MHz; 185 K) of the reaction of $CH_3CNW(CO)_5$ with $[NO][BF_4]$ in CD_2Cl_2. The base-line ripples in the full spectrum are due to elimination of the first nine points of the free induction decay (36 μs) in order to eliminate a broad signal (−180 ppm, $\nu_{1/2}$ ~15 000 Hz) due to fluorine in the NMR probe.[9b] The quartets due to **1** (−219 ppm), **3** (−203 ppm), and **5** (−238 ppm) are plotted at one-fifth the expansion of the ^{10}B (marked as **1**, **3**, and **5** in the blackened circles) and ^{11}B (marked as **1**, **3**, and **5** in the open circles) doublets at −153 ppm.

^{19}F NMR Spectrum. The 470-MHz ^{19}F NMR spectrum of a mixture of **1**–**5** prepared as described above exhibited only broad signals due to free $[BF_4]^-$ at 298 and 273 K. However, by 220 K resonances due to the bound anions were clearly visible, and by 185 K (Figure 4) these signals were well resolved into *doublets* ($^2J_{FF}$ = 95 ± 1 Hz) and *quartets* ($^2J_{FF}$ = 96 ± 1 Hz) assigned to the three terminal and single bridging fluorine atoms, respectively, of the $[(\mu\text{-}F)BF_3]^-$ ligand in each of **1**, **3**, and **5**, providing definitive evidence for coordination of $[BF_4]^-$. The spectrum is complicated by the presence of ^{11}B (80.3% natural abundance) and ^{10}B (19.7% natural abundance) isotopomers, however, so that *six* doublets near −153 ppm were observed but in three *sets* of doublets in roughly the expected 4:1 ratio. The chemical shifts, coupling constants, and 0.06 ppm downfield shifts of the ^{10}B isotopomers are all essentially the same as those previously reported for **11a**.[9b] Only three relatively broad quartets at −219, −203, and −238 ppm were observed for each of **1**, **3**, and **5**, respectively; again, as was the case for **11a**, which exhibited a broad quartet at −240.5 ppm, signals due to the boron isotopomers presumably overlap and are broadened by quadrupolar coupling to the trans-^{14}NO ligand. Finally, in addition to a small resonance at −147.3 ppm that was not identified, 18% of the anion was present as free $[BF_4]^-$

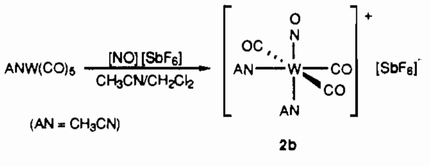
at −150.3 ppm in rough accord with the expected 9% free $[BF_4]^-$ due to **2a** measured from the ^1H NMR spectrum. While definitive assignments were made on the basis of in situ preparation of **3** and **5** via independent routes to be described below, support for the identities of the three compounds was obtained by comparison of their relative ratios to those in the ^1H NMR spectrum. Thus, as described above and in the Experimental Section, the ratio **1**:**3**:**5** was estimated from the product yields on the basis of tungsten and acetonitrile to be 72:9:19, in excellent agreement with the ratio measured from the terminal fluorine doublets in the ^{19}F NMR spectrum of 70:11:19; even the ratio estimated from the weak μ-F quartets of 74:13:13 is reasonably close.

Independent Syntheses. Once the complexity of the above reaction mixtures was fully realized, no attempt was made to separate the components; instead, independent syntheses of the various salts and $[(\mu\text{-F})BF_3]^-$ adducts were undertaken. Both infrared and ^1H NMR spectra had indicated that a pure compound, namely **4**, could be prepared by simply allowing the initial nitrosylation reaction products to stand in the presence of excess acetonitrile (eq 2). The $[SbF_6]^-$ salt **4b** was generally produced in lower albeit more reproducible yield than the $[BF_4]^-$ salt **4a**, while the $[BPh_4]^-$ salt generally allowed the easiest purification if large quantities of the dinitrosyl dications[6a,8a] formed as byproducts; **4a–c** each were isolated as yellow to orange crystalline solids in ~45–85% yields. The $[PF_6]^-$ salt **4d** was prepared for completeness, but the yield (17%) was not optimized. The stereochemistry of **4a–d** is partially evident from the ^1H and ^{13}C NMR spectra, which exhibit signals due to acetonitrile ligands in a 2:1 ratio and a single resonance for the carbon monoxide ligands. Hence, the nitrosyl ligand must be trans to the unique acetonitrile ligand. However, the equivalent acetonitrile (and carbonyl) ligands could be either cis or trans to each other. The meridional (trans) arrangement (C_{2v} point group) should give rise to one carbonyl band in the infrared, while the facial (cis) arrangement (C_s point group) should give rise to two such bands. Since two are seen, the facial stereochemistry must be present. The ions of **4a–d** are apparently tightly associated in solution, as evidenced by the lack of any fluorine signal in the room-temperature ^{19}F NMR spectrum of **4b** and by the different acetonitrile methyl resonances of **4a–d** in the ^1H NMR spectrum. In the former case, if the $[SbF_6]^-$ ion is truly spherically symmetrical, then Sb–F quadrupole coupling and concomitant broadening of the ^{19}F resonance would not be observed, hence the assumption that association must break the symmetry. In the latter case, reproducible upfield shifts of 0.01–0.02 ppm are observed on going from **4a** to **4b**. Much more strikingly, the $[BPh_4]^-$ ion acts as an internal shift reagent, giving 0.52 and 0.85 ppm upfield shifts for the six- and three-hydrogen signals of **4c**, respectively, while mixtures of **4a** and **4c** give the average positions (on the basis of the relative amounts of **4a** and **4c** present) for the two signals expected.



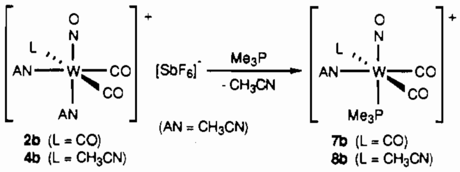
(2)

Independent synthesis of **2a** has not been accomplished. However, addition of $[NO][SbF_6]$ to $(AN)W(CO)_5$ in methylene chloride gave **2b** only as judged by ^1H NMR spectroscopy (eq 3), where signals at δ 2.60 and 2.46 ppm in a 1:1 ratio were observed, just slightly upfield (~0.01 ppm) of the $[BF_4]^-$ analogue **2a**. The origin of this result, where use of the $[BF_4]^-$ ion gives **1** as the major product, while $[SbF_6]^-$ gives only **2b**, is unknown, but the effect is curious given our finding that $[SbF_6]^-$ is clearly a better ligand than $[BF_4]^-$ for the (phosphine)tungsten nitrosyl cations shown in eq 1.[9b,12] The $[SF_6]^-$ salt **2b** could be prepared in moderate yield on a preparative scale by addition of excess acetonitrile to the methylene chloride reaction mixture. Disproportion to give some **4b** seemed to occur upon recrystallization, and attempts to purify the $[BPh_4]^-$ salt **2c** gave similar results, but despite this the noncrystalline compound **2b** (but not crystalline **2c**) could be obtained analytically pure. Ion association in **2a–c** is again evident on the basis of ^1H NMR chemical shifts; in particular **2c** exhibits upfield shifts of 0.88 and 1.22 ppm for the acetonitrile signals, although since **2c** is somewhat impure, these values may be too low. The final piece of chemical evidence for the structure of **2b** comes from allowing the isolated material to stand in acetonitrile at room temperature, which results in clean conversion to **4b**. Spectroscopically, the two acetonitrile ligands (^1H and ^{13}C NMR) and two types of carbonyl ligand in a 2:1 ratio (^{13}C NMR) are consistent only with the meridional structure shown; that is, just as in **4a–d**, one of the acetonitrile ligands is unique and so must be trans to the nitrosyl ligand.

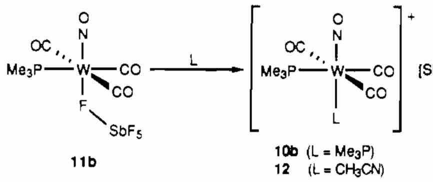


(3)

Independent syntheses of $[SbF_6]^-$ analogues of the phosphine-substituted compounds **7a**, **8a**, and **10a** were carried out in a straightforward manner. Thus, addition of Me_3P to each of **2b** and **4b** resulted in substitution of the acetonitrile ligand trans to the nitrosyl ligand, to give **7b** and **8b**, respectively (eq 4). The stereochemistry is evident in the latter case due to the equivalence of the remaining coordinated acetonitrile ligands and in the former case since the compound is *different* from the isomer (**12**) prepared from *mer*-(*cis*-Me_3P)(*trans*-NO)$(CO)_3W(\mu\text{-F})SbF_5$ (**11b**) and acetonitrile (eq 5).[9b] In addition, **7**, isomeric **12**, and **8** exhibit an unusual five-bond cis coupling constant of 1–2 Hz between the Me_3P phosphorus atom and the acetonitrile hydrogen atoms, providing further support for the relative orientation of the noncarbonyl ligands. As seen before, the ^1H NMR chemical shifts of the $[SbF_6]^-$ salts—both acetonitrile and phosphine signals—are ~0.01 ppm upfield of the $[BF_4]^-$ salts. The synthesis of **7b** also gave an unisolated and unidentified byproduct having a methylphosphine doublet (but no other identifiable signals) 0.005 ppm upfield of the signal attributed to the $[BF_4]^-$ salt **9** in Scheme II, suggesting that **2b** could be contaminated by the $[SbF_6]^-$ analogue of **6**, but further speculation on the source or identity of this signal is not warranted. The PMe_3 adduct **10b** was prepared by addition of Me_3P to **11b** (eq 5), as previously described;[9b] it too exhibits phosphine doublets ~0.01 ppm upfield of the $[BF_4]^-$ salt.

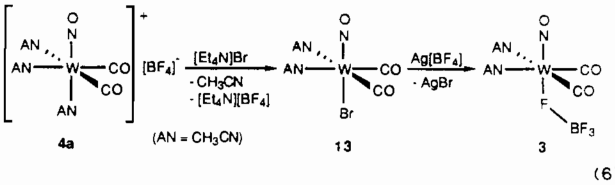


(4)



(5)

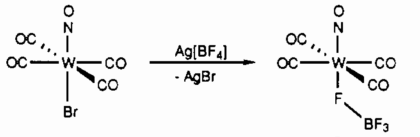
The strategy for independently synthesizing the minor $[(\mu\text{-F})BF_3]^-$ adducts proposed to be present in the nitrosylation reaction mixture involved bromide abstraction with $Ag[BF_4]$. Thus, addition of bromide to **4a** to give **13** (eq 6) resulted in displacement



(6)

of the acetonitrile ligand trans to the nitrosyl ligand, as seen previously for Me_3P (eq 4), on the basis of the ^1H NMR spectrum in which the remaining acetonitrile ligands are equivalent. Compound **13** was surprisingly difficult to purify, evidently undergoing decomposition during efforts to remove $[Et_4N][BF_4]$. Bromide abstraction with $Ag[BF_4]$ was rapid and proceeded with complete consumption of the starting material, but the reaction was not particularly clean, giving irreproducible mixtures of **1**–**4** (but on the basis of ^{13}C and ^{19}F NMR spectroscopy no **5**). Nevertheless, the results (see Experimental Section for details) clearly confirmed the identity of **3**: the major component of the reaction mixture was often that giving rise to the singlet in the ^1H NMR spectrum at δ 2.50, addition of acetonitrile immediately gave **4a** as expected, and the major $[(\mu\text{-F})BF_3]^-$ adduct in the ^{13}C and ^{19}F NMR spectra of this independently prepared material had resonances identical with those already assigned to **3**. Furthermore, the ratios of products observed in the ^1H NMR spectra were comparable to the ratios observed in the ^{13}C and ^{19}F NMR spectra, providing confirming evidence that is internally consistent with the proposed assignments. Finally, in a brief digression, the ^{19}F NMR spectrum exhibited a particularly intriguing set of $^{10}B/^{11}B$ isotopomer singlets near −150 ppm that presumably were due to "free" $[BF_4]^-$ ions—that is, ions that are not coordinated to tungsten via a (μ-F) bridge. Since there were three *sets* of these isotopomer pairs, it is difficult to resist the conclusion that each is due to a *different* ion pair; on the basis of relative intensities, two of the three free $[BF_4]^-$ ions could be assigned to **2a** (−150.37/−150.44 ppm) and to **4a** (−150.72/−150.78 ppm).

The requisite bromide to prepare **5**, *trans*-$Br(CO)_4WNO$, is known, and reaction as shown in eq 7 allowed isolation of **5** in



5

(7)

high yield as a pale yellow powder that was air- and heat-sensitive and which upon addition of excess acetonitrile immediately gave an unstable material (**6**) having bands in the infrared spectrum at 2055 (m) and 1745 (w) cm^{-1}; examination of Figure 1b indicates the nitrosyl band of **6** must be too weak to observe in this mixture. Allowing such a sample to stand for 1 h resulted in complete conversion of **6** to **4a**. The ^1H NMR spectrum confirmed both the identity of **6**, yielding a singlet at δ 2.47 that would overlap the high-field signal of **2a** as proposed, and its instability relative to **4a**. It is interesting to note that conversion of a sample prepared in situ was slower, apparently due to complexation of the acetonitrile to unreacted Ag^+. Confirmation of the identity of **5** was obtained by ^{13}C NMR spectroscopy, which at 265 K exhibited a single broad quintet at the same position assigned to **5** in the initial nitrosylation mixture, and by ^{19}F NMR spectroscopy, which similarly exhibited at 185 K peaks due to a single $[(\mu\text{-F})BF_3]^-$ ligand having chemical shifts identical with those previously assigned to **5**.

Discussion

Nitrosylations of tungsten carbonyl complexes using NO,[13] NOCl and NOBr,[8b,14] alkyl nitrites,[14c] $[NO_2]^-$,[15] and salts of $[NO]^+$, as in this work,[6a,8a,9,16] have been reported. While a rich chemistry of cyclopentadienyltungsten nitrosyls has been developed, largely by Legzdins,[17] with only a few exceptions high-yield routes to non-cyclopentadienyl nitrosyl carbonyl compounds have not been achieved. A particularly simple synthesis involves reactions of $[XW(CO)_5]^-$ (X = halide) with various nitrosonium salts to give *trans*-$XW(CO)_4NO$.[16a–c] While the initial report[16a] described the isolation of these tetracarbonyl nitrosyl compounds in high yield when the nitrosylations were carried out in methylene chloride solvent, we[18] and others[14e,16b–c] have been unable to remove the $W(CO)_6$ byproduct. Graham found that the product could be obtained free of $W(CO)_6$ by carrying out the reaction in acetonitrile, since in this solvent $W(CO)_6$ is converted to dinitrosyl dications.[6a,8a,16c] It was in fact this report that led to the results described in this paper, since one can imagine Lewis acid abstraction of halide[19] by $[NO]^+$ from $[BrW(CO)_5]^-$ to give $CH_3CNW(CO)_5$ and NOBr, with the neutral acetonitrile adduct then undergoing nitrosylation by the more abundant $[NO]^+$ starting material. Examination by IR spectroscopy of a nitrosylation reaction mixture of $[BrW(CO)_5]^-$ in acetonitrile in fact revealed a complex mixture of products, but while some **4** could have been present, it was not a major product. The mononitrosyl halides can be obtained in ~20% yields by this route, but we have been unable to scale up this reaction. In practice, where subsequent reactions allow convenient removal of $W(CO)_6$, as described here for **5** and previously for a Diels–Alder catalyst precursor containing a chelating phosphine ligand,[18] the methylene chloride route is preferred.

The cleanest high-yield chemistry that results in mononitrosyl carbonyl compounds appears to be that using $[NO]^+$ with compounds containing (1) chelating N-donor ligands or chelating phosphines, including Connelly's reports on 2,2′-bipyridine, 1,10-phenanthroline, and 1,2-bis(diphenylphosphino)ethane compounds[16d,e] as well as Connor's related alkylphosphine chelates,[16f] (2) two phosphine or phosphite ligands, as seen in Berke's report on *cis*-$\{(RO)_3P\}_2W(CO)_4$[16g] and Hillhouse and Haymore's detailed description of the nitrosylation of *cis*- or *trans*-$(Ph_3P)_2W(CO)_4$,[16h] and (3) a single strong donor[10] phosphine ligand ($R_3P \neq Ph_3P$), as seen in our work starting with $R_3PW(CO)_5$ (eq 1);[9] in all of these examples[9,16d–h] *tri*carbonyl compounds were obtained. We have suggested that formation of *mono*nitrosyl compounds may be governed by the σ-donor/π-acceptor properties[10] of the ligands on tungsten, since $W(CO)_6$ and $Ph_3PW(CO)_5$ apparently yield dinitrosyl dications,[9b] in contrast to the above more electron-rich compounds with N-donor ligands, *two* phosphine ligands, or *alkyl*phosphine ligands. Clearly, the reactions of $CH_3CNW(CO)_5$ described here fit this mononitrosylation hypothesis. It is interesting to note, however, that electron density on tungsten is not the sole determinant of degree of nitrosylation, since reaction of *fac*-$(CH_3CN)_3W(CO)_3$ with $[NO]^+$ gives only *di*nitrosyl dications and no **4**;[8a] this result further suggests that **4** is *not* an intermediate in the nitrosylation of $(CH_3CN)_3W(CO)_3$, posing an interesting mechanistic question.

In conclusion, nitrosylation of $CH_3CNW(CO)_5$ with $[NO][BF_4]$ yields a complex mixture of five products, which have been identified by a combination of spectroscopic methods, quantitative results on reactions of the compounds in the mixture with acetonitrile and trimethylphosphine, and independent syntheses. The

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major initial nitrosylation product is the $[(\mu\text{-F})BF_3]^-$ adduct **1**, which was unambiguously characterized by a combination of ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy and its conversion to **2a**. Generation via bromide abstraction and subsequent ^{13}C and ^{19}F NMR observation of the minor $[(\mu\text{-F})BF_3]^-$ adducts **3** and **5** allowed the unambiguous characterization of these labile materials. No attempt was made to independently generate **1**, which in principle might have been done from **2** in analogy to the synthesis of **3** via **13** from **4a**, due to the difficulty associated with the synthesis of **13** as well as the fact that the identity of **1** is not in doubt. From a synthetic point of view, the initial nitrosylation mixture of **1–5** does not appear likely to find much use, given the separation problems inherent in any subsequent reactions, although it is conceivable that the ~60% yield of *mer*-adducts **1** and **2a** could lead to an isolable product. While the independent synthesis of *mer*-adduct **2b** has been achieved, the yield is relatively low. Of the $[(\mu\text{-F})BF_3]^-$ adducts, **5** is the most appealing due to its simplicity and ease of preparation, although future work will focus on what we expect to be the more stable[9b,12] $[(\mu\text{-F})SbF_5]^-$ adduct. Most importantly, a convenient and large scale synthesis of the new cation $[fac\text{-}(CH_3CN)_3W(CO)_2NO]^+$ is now available, which by analogy to the chemistry of $fac\text{-}(CH_3CN)_3W(CO)_3$[20] should serve as a useful building block in the synthesis of novel tungsten nitrosyl compounds; already one effort in cluster synthesis has been successful and will be reported in due course.[21]

Experimental Section

General Procedures. All manipulations of air-sensitive compounds were carried out either in a Vacuum Atmospheres inert atmosphere drybox under recirculating nitrogen or by use of standard Schlenk techniques. NMR spectra were recorded on JEOL FX90Q (^{1}H, ^{13}C, ^{19}F, ^{31}P) and Bruker WP-200 (^{1}H) and AM-500 (^{1}H, ^{13}C, ^{19}F) spectrometers; chemical shifts are reported relative to residual $CHDCl_2$ at δ 5.32 in CD_2Cl_2 (^{1}H), to CD_2Cl_2 at 53.8 ppm (^{13}C), and to external $CFCl_3$ and 8.5% H_3PO_4 (in coaxial capillary tubes) at 0.0 ppm (^{19}F, ^{31}P). Infrared spectra were obtained on a Perkin-Elmer 237 spectrometer with 0.1-mm NaCl solution cells. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

All solvents were treated under nitrogen. Acetonitrile was purified by sequential distillation from calcium hydride and phosphorus pentoxide. Diethyl ether, dioxane, and tetrahydrofuran were distilled from sodium benzophenone ketyl. Absolute ethanol was purged with nitrogen over 4-Å molecular sieves. Hexanes (Fisher, mixture of isomers, bp 68.5–69.4 °C) was purified by washing successively with 5% nitric acid in sulfuric acid, water, sodium bicarbonate solution, and water and then dried over calcium chloride and distilled from *n*-butyllithium in hexane. Methylene chloride and 1,1,2-trichlorotrifluoroethane were distilled from phosphorus pentoxide; CD_2Cl_2 was vacuum-transferred from phosphorus pentoxide.

Tungsten hexacarbonyl either was used unsublimed, as received from Pressure Chemical Co., or was used sublimed, as noted below. Nitrosonium tetrafluoroborate (Aldrich) and hexafluorophosphate (Alfa) were sublimed at 160 °C, 6×10^{-4} mmHg. Trimethylphosphine (Strem), $NaBPh_4$ (Aldrich), $AgBF_4$, and $[NO][SbF_6]$ (Ozark-Mahoning) were used as received.

$[(CH_3CH_2)_4N][BrW(CO)_5]$. This compound was prepared by using a modification of the standard procedure.[22] Sublimed $W(CO)_6$ (50.0 g, 142 mmol) and oven-dried $[(CH_3CH_2)_4N]Br$ (29.0 g, 140 mmol) were heated at reflux in 500 mL of dioxane for 2 h. After cooling, 100 mL of petroleum ether was added (in the air), and the yellow solid was broken up and washed with 200 mL of more petroleum ether. The solid was heated (60 °C) under vacuum for 2 h to remove unreacted $W(CO)_6$ and taken up in 400 mL of THF under nitrogen, and the mixture was filtered and stripped to give 71.4 g (97% yield) of product as a bright yellow powder.

$CH_3CNW(CO)_5$. Method A. Pure material that was used for the NMR experiments was prepared in roughly 3-g quantities in 80% yield by a modification of Schenk's procedure:[23] the reaction was carried out for 2 h at room temperature, the product that was precipitated with water was dried and taken up in ether, and the mixture was filtered through alumina.

Method B. Except as noted, all preparative reactions used material prepared by this method. Unsublimed $W(CO)_6$ (11.5 g, 32.7 mmol) and 200 mL of undistilled acetonitrile were combined in the air and purged briefly with nitrogen. To this suspension was added 3.68 g (33.1 mmol) of $Me_3NO{\cdot}2H_2O$. The mixture immediately turned yellow and was stirred rapidly under aspirator vacuum for 5 min. After an additional 5 min under nitrogen, most of the solid had dissolved. The solution was filtered in the air and the solvent removed on a vacuum line. The yellow powder was taken up in 50 mL of acetonitrile under nitrogen, and the solution was filtered through a 20-mL pad of silica gel and washed with 30 mL of more acetonitrile. After solvent removal, 10.66 g (89% yield) of yellow powder was obtained. This material typically consisted of 92.5–94 mol % $CH_3CNW(CO)_5$ (δ 2.292 in CD_2Cl_2) and 6–7.5 mol % $Me_3NW(CO)_5$ (δ 2.975 in CD_2Cl_2) but despite the impurity was found to be a convenient source of starting material.

[*mer,cis*-$(CH_3CN)_2W(CO)_3(NO)$][SbF_6] (2b). A solution of 146 mg (0.549 mmol) of $[NO][SbF_6]$ in 0.25 mL of acetonitrile was added dropwise to a −40 °C solution of $CH_3CNW(CO)_5$ (method A; 199 mg, 0.545 mmol) in 3 g of a 10:1 (wt:wt) mixture of methylene chloride/acetonitrile. Bubbling and a flash of red color were observed as each drop of $[NO][SbF_6]$ solution was mixed in. Following the addition, 30 mL of hexanes was added to the yellow-orange suspension to complete precipitation of the product, and the solvent was removed in vacuo. The residue was washed with 1,1,2-trichlorotrifluoroethane and then hexanes to remove unreacted starting material, and the light yellow powder was extracted with 2 × 10 mL of methylene chloride. Crystallization at −35 °C followed by recrystallization in 10 mL of CH_2Cl_2 gave 114 mg (34% yield) of product as a bright yellow powder. IR (CH_2Cl_2): 2330 (w), 2282 (w), 2114 (w), 2059 (m), 2033 (s), 1999 (ms), 1719 cm^{-1} (ms). ^{1}H NMR (CD_2Cl_2): δ 2.599 (s, 3 H, CH_3CN cis to NO), 2.457 (s, 3 H, CH_3CN trans to NO). ^{13}C NMR (CD_2Cl_2): 204.24 ($^1J_{CW}$ = 165.7 Hz, CO trans to CH_3CN), 194.95 ($^1J_{CW}$ = 139.0 Hz, *trans*-$(CO)_2$), 131.10, 4.15 (CH_3CN cis to NO), 125.72, 3.72 ppm (CH_3CN trans to NO). Anal. Calcd for $C_7H_6N_3O_4F_6SbW$: C, 13.65; H, 0.98; N, 6.82. Found: C, 13.57; H, 0.98; N, 6.78. The ^{1}H NMR spectrum reproducibly indicated the presence of ~10% of **4b**, so it is likely that disproportionation occurs in solution.

[*mer,cis*-$(CH_3CN)_2W(CO)_3(NO)$][$(C_6H_5)_4B$] (2c). A mixture of 101 mg (0.16 mmol) of **2b** and 112 mg (0.33 mmol) of $Na[(C_6H_5)_4B]$ in 2 mL of methylene chloride was stirred for 3 h, filtered, and cooled to −35 °C. Hexanes (1 mL) was layered on, and 88 mg of yellow crystals were obtained. ^{1}H NMR spectroscopy indicated the presence of **4c**, so the product was recrystallized; nonetheless, a 7% impurity of **4c** remained. IR (CH_2Cl_2): 2105 (w), 2020 (s), 2000 (s), 1945 (w), 1610 cm^{-1} (s). ^{1}H NMR (CD_2Cl_2): δ 6.9–7.4 (m, 20 H), 1.720 (s, 3 H), 1.238 (s, 3 H). Anal. Calcd for $C_{31}H_{26}N_3O_4BW$: C, 53.25; H, 3.75; N, 6.01. Found: C, 50.10; H, 3.70; N, 5.87.

***cis,cis,trans*-$(CH_3CN)_2(CO)_2(NO)W(\mu\text{-F})BF_3$ (3).** A solution of 172 mg (0.82 mmol) of oven-dried $[(CH_3CH_2)_4N]Br$ in 3 mL of CH_2Cl_2 was added to 402 mg (0.84 mmol) of **4a** in 5 mL of CH_2Cl_2. After being stirred for 10 min, the solution was concentrated and 10 mL of hexanes added to precipitate the intermediate bromide *cis,cis,trans*-$(CH_3CN)_2(CO)_2(NO)WBr$ (**13**). This material was taken up in 20 mL of CH_2Cl_2, the solution filtered though a 5-mL pad of neutrai alumina II and concentrated, and **13** reprecipitated with hexanes to give 250 mg of a yellow solid; this material typically still contained ~25% $[(CH_3CH_2)_4N]^+$ by ^{1}H NMR spectroscopy. Washing with 150 mL of water gave 75 mg of material, which was taken up in the minimum amount of CH_2Cl_2 (1.5 mL). The solution was filtered, and the solid was precipitated with 1.5 mL of hexanes to give 48 mg (14% yield) of **13** (which still contained 0.8 mol % of $[(CH_3CH_2)_4N]^+$) as a yellow noncrystalline solid. IR (CH_2Cl_2): 2015 (s), 1930 (s), 1630 cm^{-1} (m). ^{1}H NMR (CD_2Cl_2): δ 2.480 (s). Samples of **3** were prepared in situ (no elemental analyses on **3** or **13** were obtained) by vigorous stirring of a suspension of **13** and 1.5 equiv of $AgBF_4$ in CD_2Cl_2 for ~5 min followed by filtration of the gray AgBr with Celite to give a dark orange-yellow solution. Analysis by ^{1}H NMR spectroscopy gave variable mixtures of **1–4**, but typically the major peak was the singlet at δ ~2.504 due to **3**; addition of CH_3CN gave **2a** and **4a** in the expected ratios. ^{13}C NMR (265 K, 5:5:72:18 mixture of **1–4**): 214.40 (quintet, $^2J_{CF}$ = 6.5 Hz, $(CO)_2$), 126.34 ($CH_3\mathit{C}N$), 3.92 ppm ($\mathit{C}H_3CN$) (**3**, major bands); 213.06 ($(CO)_2$), 127.60, 3.60 ($(CH_3CN)_2$ cis to NO), 122.73, 3.14 ppm (CH_3CN trans to NO) (**4a**, minor bands); 200.24 (small unidentified singlet), 194.87 (small, (*trans*-$(CO)_2$ of **2a**),125.50, 4.23 ppm, (**2a**); 3.92, 3.55, 3.43 ppm (small unidentified CH_3CN bands). ^{19}F NMR (185 K, 9:13:20:58 mixture of **1–4** and 32:68 mixture of **1** and **3**): −152.96 (d, $^2J_{FF}$ = 93.5 Hz, ^{10}B), −153.03 (d, $^2J_{FF}$ = 93.6 Hz, ^{11}B), −202.78 ppm (q, $^2J_{FF}$ = 93.2 ± 0.8 Hz) (**3**, 14%); −153.11 (d, $^2J_{FF}$ = 94.5 Hz, ^{11}B; ^{10}B overlaps with **3**), −219.29

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(20) See for instance: (a) Tate, D. P.; Augl, J. M. *J. Am. Chem. Soc.* **1963**, *85*, 2174–2175. (b) King, R. B.; Fronzaglia, A. *Inorg. Chem.* **1966**, *5*, 1837–1846. (c) Horwitz, C. P.; Holt, E. M.; Shriver, D. F. *Ibid.* **1984**, *23*, 2491–2499. (d) Hriljac, J. A.; Holt, E. M.; Shriver, D. F. *Ibid.* **1987**, *26*, 2943–2949.

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ppm (q, $^2J_{FF}$ = 95.2 ± 1.6 Hz) (**1**, 4%); −149.03, −149.10 (^{10}B, ^{11}B [BF$_4$]$^-$ ion pair, 8%), −150.37, −150.44 ppm (^{10}B, ^{11}B [BF$_4$]$^-$ ion pair, 17%, possibly **2a**); −150.72, −150.78 ppm (^{10}B, ^{11}B [BF$_4$]$^-$ ion pair; 58%, possibly **4a**).

[*fac*-(CH$_3$CN)$_3$W(CO)$_2$(NO)][BF$_4$] (4a). Powdered, sublimed [NO][BF$_4$] (0.38 g, 3.25 mmol) was added in one portion to a solution of 1.00 g (2.74 mmol) of CH$_3$CNW(CO)$_5$ and 0.48 g (11.7 mmol) of CH$_3$CN in 15 mL of CH$_2$Cl$_2$. The yellow solution bubbled vigorously for 5 min, as the [NO][BF$_4$] dissolved, and then very slowly over the next 15 min, as the solution began to acquire a green tint. After filtration through a pad of Celite and solvent removal, the resultant yellow solid was taken up in 20 mL of acetonitrile and allowed to stand overnight; slow bubbling was observed as the green yellow solution turned orange yellow. The solvent was then removed on a vacuum line, and the yellow solid was taken up in 15 mL of CH$_2$Cl$_2$. The solution was filtered and cooled to −35 °C. A 10-mL layer of ether was then placed on the cold solution and allowed to diffuse in overnight. The resultant solid was filtered out and washed with ether and hexanes. Three crops of a fluffy yellow solid were obtained, giving 1.14 g (87% yield) of product. IR (CH$_2$Cl$_2$): 2320 (w), 2294 (mw), 2028 (s), 1945 (s), 1683 cm^{-1} (s). ^{1}H NMR (CD$_2$Cl$_2$): δ, 2.547 (s, 6 H), 2.417 (s, 3 H). ^{19}F NMR (CD$_2$Cl$_2$, −70 °C, 84 MHz): −151.51 ppm. ^{19}F NMR (CD$_2$Cl$_2$, 298 K, 475 MHz): −152.65 ppm. Anal. Calcd for C$_8$H$_9$N$_4$O$_3$F$_4$BW: C, 20.03; H, 1.89; N, 11.68. Found: C, 19.82; H, 1.74; N, 11.54.

[*fac*-(CH$_3$CN)$_3$W(CO)$_2$(NO)][SbF$_6$] (4b). A solution of 3.85 g (14.5 mmol) of [NO][SbF$_6$] in 8 mL of acetonitrile was added dropwise over 1 min to a solution of 5.02 g (13.8 mmol) of CH$_3$CNW(CO)$_5$ in 50 mL of acetonitrile. The yellow solution typically turns red immediately and then turns dark green at an irreproducible time (from nearly immediately to halfway through the addition); carbon monoxide evolves at a moderate rate during the addition. The reaction may be monitored by IR spectroscopy to observe the conversion of immediately formed **2b** to **4b**, but it is typically done in 1.5–3 h. The solvent was removed on a vacuum line and the gummy green residue washed with 100 mL of 1:1 hexane/ether to remove starting material. The residue was then taken up in 25 mL of methylene chloride, and 60 mL of ether was added. A cloudy orange supernatant formed over a green oil. The solution was filtered through Celite, and the green oil was treated nine more times sequentially with increasingly smaller amounts of methylene chloride followed by ether, in a 1:2 ratio, giving ~150 mL of solution. After the seventh treatment, the green oil solidified to give a green powder; after the final extraction 2.3 g of this unidentified material (presumably consisting of dinitrosyl dications) remained. The orange supernatant was cooled to −35 °C and gave, in four crystallizations, 4.03 g (47% yield) of analytically pure product as blocky orange crystals. IR (CH$_2$Cl$_2$): 2027 (s), 1946 (s), 1685 cm^{-1} (s). ^{1}H NMR (CD$_2$Cl$_2$): δ 2.530 (s, 6 H), 2.394 (s, 3 H). ^{13}C NMR (CD$_2$Cl$_2$): 213.03 ($^1J_{CW}$ = 177.8 Hz, (CO)$_2$), 127.71, 3.60 ((CH$_3$CN)$_2$ cis to NO), 122.85, 3.05 ppm (CH$_3$CN trans to NO). Anal. Calcd for C$_8$H$_9$N$_4$O$_3$F$_6$SbW: C, 15.28; H, 1.44; N, 8.91. Found: C, 15.15; H, 1.35; N, 8.72.

[*fac*-(CH$_3$CN)$_3$W(CO)$_2$NO][(C$_6$H$_5$)$_4$B] (4c). Solid powdered [NO][SbF$_6$] (0.73 g, 2.75 mmol) was added in small portions, with a few seconds of waiting for the bubbling to subside between additions, to a solution of 1.02 g (2.79 mmol) of CH$_3$CNW(CO)$_5$ in 10 mL of acetonitrile. Irreproducible color changes were observe as described above in the synthesis of **4b**. After the green solution was allowed to stand overnight, 0.94 g (2.75 mmol) of NaBPh$_4$ was added, and the still homogeneous solution cooled to −35 °C. After 4 h, the solution was filtered to give 2.19 g of yellow powder; a second 0.23-g crop was obtained following concentration of the acetonitrile solution to 5 mL. The yield of crude product, if it contains 1 full equiv of NaSbF$_6$ as expected, is quantitative. After washing with hexanes, the product was extracted in three portions with a total of 175 mL of CH$_2$Cl$_2$, and the solvent was removed on a vacuum line. The yellow powder was recrystallized from 15 mL of acetonitrile at −35 °C, giving 0.56 g of a yellow fine crystalline solid. A second crop of 0.29 g (50% overall yield) was obtained by reextracting all residues with CH$_2$Cl$_2$ and recrystallizing from acetonitrile. IR (CH$_2$Cl$_2$): 2028 (m), 1941 (m), 1688 cm^{-1} (m). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.40 (br m, 8 H), 7.04 (t, J = 7.3 Hz, 8 H), 6.89 (t, J = 7.3 Hz, 4 H), 2.015 (s, 6 H), 1.555 (s, 3 H). Anal. Calcd for C$_{32}$H$_{29}$N$_4$O$_3$BW: C, 53.96; H, 4.10; N, 7.87. Found: C, 53.83; H, 4.23; N, 8.19.

[*fac*-(CH$_3$CN)$_3$W(CO)$_2$NO][PF$_6$] (4d). Solid [NO][PF$_6$] (0.50 g, 2.86 mmol) was added in two portions to a solution of 1.00 g (2.74 mmol) of CH$_3$CNW(CO)$_5$ and 0.44 g of CH$_3$CN (10.7 mmol) in 15 mL of CH$_2$Cl$_2$. Immediate but transient vigorous bubbling was observed. The solution gradually turned brown-orange over 15 min, but IR spectroscopy indicated the presence of **4d**, the diacetonitrile adduct, and a large amount of unreacted starting material. After stirring for 1 h followed by addition of 1 mL of acetonitrile and stirring for 1 h more, the mixture was filtered and the solvent removed. The resulting yellow oil was taken up in 15 mL of acetonitrile and allowed to stand overnight. Following solvent removal, the orange solid was washed with benzene and then hexanes to give 224 mg of spectroscopically pure product. Addition of hexanes to the benzene wash precipitated out 119 mg of material, which after washing with 10 mL of 1:1 benzene/hexanes yielded 100 mg of product that was combined with the above 224-mg fraction. Solvent removal from the wash solutions yielded 0.51 g of recovered CH$_3$CNW(CO)$_5$. The 324 mg of product was crystallized with difficulty by layering 0.5 mL of ether onto 2 mL of a cold 1:1 CH$_2$Cl$_2$/ether solution at −35 °C, giving 125 mg (17% yield based on recovered starting material) of orange crystals. IR (CH$_2$Cl$_2$): 2310 (w), 2279 (w), 2026 (s), 1941 (s), 1683 cm^{-1} (s). ^{1}H NMR (CD$_2$Cl$_2$): δ 2.529 (s, 6 H), 2.395 (s, 3 H). ^{19}F NMR (CD$_2$Cl$_2$): −72.48 ppm (d, $^1J_{PF}$ = 708 Hz). ^{31}P NMR (CD$_2$Cl$_2$): −144.46 ppm (septet, $^1J_{PF}$ = 709 Hz). Anal. Calcd for C$_8$H$_9$N$_4$O$_3$F$_6$PW: C, 17.86; H, 1.69; N, 10.41. Found: C, 17.89; H, 1.64; N, 10.10.

***trans*-(CO)$_4$(NO)W(μ-F)BF$_3$ (5).** The starting material *trans*-BrW(CO)$_4$(NO) was conveniently prepared on a reasonable scale by reaction of 4–5 g of [(CH$_3$CH$_2$)$_4$N][BrW(CO)$_5$] with 1 equiv of [NO][SbF$_6$] in CH$_2$Cl$_2$;[16a] typically, yields were 40–50% following chromatography. The product was contaminated by ~25–28% W(CO)$_6$, as judged by elemental analysis, but this had no obvious effect on the bromide abstraction reaction. To a vigorously stirred solution of 206 mg of this material (containing 0.376 mmol of bromide assuming 74% purity) in 10 mL of CH$_2$Cl$_2$ was added 103 mg (0.53 mmol) of AgBF$_4$ in one portion. A white suspension formed immediately, and over the course of 10 min the mixture turned cloudy gray in appearance. Filtration through Celite gave a yellow solution that exhibited a very clean sharp IR spectrum (2055 (s), 1725 (m) cm^{-1}; ν(W(CO)$_6$) at 1970 (s) cm^{-1}) that differed slightly from that of the starting material (2045, 1700 cm^{-1}). The solvent was rapidly removed at a vacuum of <10^{-3} mmHg, and the resultant pale yellow powder further warmed at ~40 °C (2 × 10^{-4} mmHg) for a few minutes to remove some W(CO)$_6$, giving 133 mg (86% yield, assuming a negligible amount of W(CO)$_6$) of **5**. The compound turns black on exposure to air and rapidly decomposes on standing at room temperature, as judged by formation of cloudy CH$_2$Cl$_2$ solutions upon immediately redissolving this material (which nevertheless has the same IR spectrum as noted above); overnight storage at −40 °C also results in formation of a substantial amount of black CH$_2$Cl$_2$-insoluble material. Addition of acetonitrile to a freshly prepared sample of solid **5** immediately gave bands assigned to **6** (2055 (m), 1745 (w) cm^{-1}), and on standing 1 h the sample was completely converted to **4a**. Samples for ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy were prepared in situ as above but with 1.5–1.9 equiv of AgBF$_4$ in CD$_2$Cl$_2$. Addition of excess acetonitrile to such a sample gave a singlet at δ 2.467 (**6**) and a broad singlet at δ 2.06 rather than 1.97 for "free" acetonitrile, suggesting the presence of dissolved Ag$^+$. After 40 min at room temperature, the sample contained **2a**, **4a**, and **6** in the ratio 28:6:65. ^{13}C NMR (265 K): 193.31 ppm (broad quintet, apparent $^2J_{CF} \approx$ 4.7 Hz). ^{19}F NMR (185 K): −153.12 (d, $^2J_{FF}$ = 95.0 Hz, ^{10}B), −153.18 (d, $^2J_{FF}$ = 95.2 Hz, ^{11}B), −238.33 ppm (q, $^2J_{FF}$ = 95.9 ± 1.0 Hz) (**5**); −147.86, −149.62 (minor [BF$_4$]$^-$ ^{11}B singlets with poorly resolved ^{10}B singlets ~0.06 ppm downfield), −151.87 ppm (s, $\nu_{1/2}$ = 70 Hz, free [BF$_4$]$^-$, comparable height to that of the [(μ-F)BF_3]$^-$ doublet of **5** having $\nu_{1/2}$ = 10 Hz).

[*mer*-(*cis*-CH$_3$CN)(*trans*-Me$_3$P)W(CO)$_3$(NO)][SbF$_6$] (7b). A solution of 25 mg (0.33 mmol) of Me$_3$P in 1 mL of methylene chloride was added in one portion to a yellow suspension of **2b** (185 mg, 0.30 mmol) in 6 mL of methylene chloride. The solid immediately dissolved, giving an orange solution. The solvent was removed and the resultant yellow powder crystallized from 2 mL of methylene chloride at −35 °C; a second crop was obtained from 0.5 mL of methylene chloride, to give a total of 76 mg (39% yield) of yellow-orange crystals. IR (CH$_2$Cl$_2$): 2095 (w), 2075 (w), 2045 (m, sh), 2015 (s), 1980 (m), 1715 cm^{-1} (m). ^{1}H NMR (CD$_2$Cl$_2$): δ 2.650 (d, $^5J_{PH}$ = 1.22 Hz, 3 H), 1.656 (d, $^2J_{PH}$ = 9.16 Hz, 9 H). An unidentified phosphine impurity (see text) appearing at δ 1.780 (d, $^2J_{PH}$ = 9.46 Hz), amounting to 15% of the total, could not be removed by recrystallization; no elemental analysis was attempted.

[*mer*-(*cis*-CH$_3$CN)(*trans*-Me$_3$P)W(CO)$_3$(NO)][(C$_6$H$_5$)$_4$B] (7c). A mixture of **7b** (25 mg) and excess Na[(C$_6$H$_5$)$_4$B] (60 mg) was stirred in 1 mL of methylene chloride for 3 h and filtered, and the solution was cooled to −35 °C. Hexanes (1 mL) was layered on, and after standing overnight at −35 °C, the solution yielded 18 mg (64% yield) of bright orange needles. IR (CH$_2$Cl$_2$): 2095 (w), 2045 (m), 2010 (s), 1995 (m), 1724 cm^{-1} (m). ^{1}H NMR (CD$_2$Cl$_2$): δ 6.9–7.4 (m, 20 H), 1.819 (d, $^5J_{PH}$ = 1.27 Hz, 3 H), 1.482 (d, $^2J_{PH}$ = 8.90 Hz, 9 H), 1.420 (d, $^2J_{PH}$ = 9.23 Hz, 7.3% impurity). Anal. Calcd for C$_{32}$H$_{32}$N$_2$O$_4$BPW: C, 52.35; H, 4.39; N, 3.82. Found: C, 52.17; H, 4.28; N, 3.77.

[*cis,cis,trans*-(CH$_3$CN)$_2$(CO)$_2$(NO)W(PMe$_3$)][SbF$_6$] (8b). A solution of 61 mg (0.80 mmol) of Me$_3$P in 0.5 mL of methylene chloride was added in one portion to an orange solution of **4b** (443 mg, 0.70 mmol) in 5 mL of methylene chloride. The red-orange solution was immediately pumped dry, giving a red-orange crystalline solid that was taken up in 4 mL of methylene chloride. The solution was filtered and the filtrate cooled to −35 °C. An equal volume of hexanes was layered on, and after standing 1.5 h at −35 °C, the solution yielded 410 mg of crystals. ^{1}H NMR spectroscopy revealed the presence of **4b** and two unidentified phosphine doublets as impurities, so the compound was recrystallized as above from 1.5 mL each of methylene chloride and hexanes, giving 336 mg (72% yield) of large red-orange crystals. IR (CH_2Cl_2): 2010 (s), 1925 (s), 1685 cm^{-1} (s). ^{1}H NMR (CD_2Cl_2): δ, 2.585 (d, $^5J_{PH} = 1.53$ Hz, 6 H), 1.510 (d, $^2J_{PH} = 8.85$ Hz, 9 H), 1.639 (d, $^2J_{PH} = 8.85$ Hz, 4% impurity). Anal. Calcd for $C_9H_{15}N_3O_3F_6PSbW$: C, 16.28; H, 2.28; N, 6.33. Found: C, 16.25; H, 2.23; N, 6.29.

Infrared Experiments. Powdered [NO][BF_4] (12.8 mg, 0.110 mmol) was added to a rapidly stirred solution of 31.7 mg (0.0869 mmol) of $CH_3CNW(CO)_5$ (method A) in 1.45 g (1.09 mL, 0.08 M solution) of CH_2Cl_2. The [NO][BF_4] dissolved in ~5 min, after which the evolution of CO stopped. The yellow solution was filtered through glass wool, and the IR spectrum recorded (Figure 1a). To a 0.22-g portion of this solution was added ~1.5 μL of CH_3CN (~1.18 mg, 0.029 mmol, ~2.2 equiv), and the IR spectrum of the slightly darker yellow solution was recorded (Figure 1b). After 4 h, the color was orange, and the IR spectrum was again recorded (Figure 1c). The portion to which no CH_3CN had been added turned orange with formation of a brown precipitate after 4 h. IR: 2115 (w), 2099 (w), 2045 (ms), 2000 (sh, m), 1945 (m), 1710 (m), 1690 cm^{-1} (m).

^{1}H NMR Experiments. In one set of experiments, powdered [NO][BF_4] (14.4 mg, 0.123 mmol) was added to a rapidly stirred solution of $CH_3CNW(CO)_5$ (31.4 mg, 0.086 mmol; method A) in ~1 mL of CD_2Cl_2. The green-yellow solution was filtered through glass wool, and 9.0 μL (11.116 mg, 0.1123 mmol) of 1,2-dichloroethane was added as an internal integration standard. The solution was split approximately in half, and 5.4 μL (4.24 mg, 0.103 mmol, ~2.4 equiv) of acetonitrile was added to one NMR tube. Both tubes were centrifuged and stored at 0 °C prior to recording (within 0.5 h of preparation) the ^{1}H NMR spectra. The tube without CH_3CN contained **1** (δ 2.572; 0.0363 ± 0.0008 mmol), **2a** (δ 2.592 (3 H), 2.448 (3 H); 0.0106 ± 0.0001 mmol), **3** (δ 2.502; 0.0085 ± 0.0005 mmol), and **4a** (δ 2.532 (6 H), 2.398 (3 H); 0.000 96 ± 0.000 14 mmol); deviations were derived from two measurements of the integrals and do not reflect possible errors in the measured quantities of $CH_3CNW(CO)_5$ or $ClCH_2CH_2Cl$. The tube with CH_3CN contained **2a** (δ 2.606, 2.466; 0.0470 ± 0.0006 mmol), **4a** (δ 2.544, 2.412; 0.0166 ± 0.0014 mmol), and **6** (δ 2.466; 0.0142 ± 0.0019 mmol). After 24 h, this latter tube contained only **4a** (δ 2.543, 2.411; 0.0815 ± 0.0027 mmol), while the tube without CH_3CN contained **1** (0.0318 mmol), **2a** (0.0132 mmol), **3** (0.0059 mmol), **4a** (0.0027 mmol), and **6** (0.0008 mmol).

In a second set of ^{1}H NMR experiments in which no internal integration standard was used, 21 mg (0.180 mmol) of [NO][BF_4] and 58 mg (0.159 mmol) of $CH_3CNW(CO)_5$ (method A) were combined in ~1.5 mL of CD_2Cl_2, and 4 μL (0.077 mmol) of CH_3CN was added to one-third of this solution to give a 69.7:14.1:16.2 mixture of **2a**, **4**, and **6**. On the basis of the assumption that 16.2% of the sample prior to addition of CH_3CN contained **5**, the original sample was calculated to contain **1–5** in a ratio of 51.9:19.4:10.6:1.9:16.2. To this original mixture (again about one-third of the sample) was added 4 μL (0.039 mmol) of Me_3P, giving **1** (1.9%; δ 2.580), **2a** (15.5%; δ 2.607, 2.466), **3** (2.3%; δ 2.510), **4a** (4.1%; δ 2.510, 2.413), **7a** (59.2%; δ 2.661 (d, $^5J_{PH} = 1.3$ Hz, 3 H), 1.667 (d, $^2J_{PH} = 9.2$ Hz, 9 H)), **8a** (6.3%; δ 2.597 (d, $^5J_{PH} = 1.3$ Hz, 6 H), 1.519 (d, $^2J_{PH} = 8.9$ Hz, 9 H)), and **9** (10.6%; δ 1.785 (d, $^2J_{PH} = 9.9$ Hz); these percentages give 0.76 equiv of Me_3P added. Finally, excess Me_3P (1 drop) was added to the final one-third portion of the original nitrosylation mixture (which had stood at room temperature for ~1 h), giving **7a** (35.3%), **8a** (11.2%), **9** (11.1%), **10a** (42.4%; δ 1.878 (d, $^2J_{PH} = 8.9$ Hz), 1.687 (d, $^2J_{PH} = 8.9$ Hz)), a number of smaller unidentifiable peaks at δ 1.7–1.4, free CH_3CN (δ 1.970), and free Me_3P (δ 1.006); the amount of free Me_3P gives ~2 equiv added.

^{13}C NMR Experiment. Powdered [NO][BF_4] (102 mg, 0.87 mmol) was added to 245 mg (0.67 mmol) of $CH_3CNW(CO)_5$ (method A) dissolved in 3 mL of CD_2Cl_2. After filtration into a 10-mm NMR tube, additional CD_2Cl_2 was added to give a total volume of 3.6 mL (~0.19 M solution). The ^{13}C NMR spectrum (125 MHz) was run at 265 K as well as for a shorter time at 208 K; only for the former spectrum was the signal to noise ratio high enough to observe the ^{183}W (14% natural abundance, $I = {}^1/_2$) satellites on the carbonyl peaks. In the following list, q refers to quintet, while all other peaks are singlets, and percentages were determined by relative integration of the carbonyl region of the spectrum; where comparable, similar ratios were derived from the CH_3CN peaks. ^{13}C NMR (265 K): 206.13 (q, $^2J_{CF} = 8.1$ Hz, $^1J_{CW} = 173.8$ Hz, CO trans to CH_3CN), 197.40 (q, $^2J_{CF} = 11.4$ Hz, $^1J_{CW} = 143.9$ Hz, *trans*-$(CO)_2$), 129.84, 4.25 ppm (CH_3CN) (**1**, 64%); 204.45 ($^1J_{CW} = 165.7$ Hz, CO trans to CH_3CN), 194.97 ($^1J_{CW} = 139.0$ Hz, *trans*-$(CO)_2$), 131.07, 4.18 (CH_3CN cis to NO), 125.64, 3.74 ppm (CH_3CN trans to NO) (**2a**, 8%); 214.45 (~q, $^2J_{CF} = 8$ Hz, concentration too low to observe $^1J_{CW}$, $(CO)_2$), 126.26, 3.899 ppm ($(CH_3CN)_2$) (**3**, 5%); 193.39 ppm (br ~s, $\nu_{1/2} = 6.6$ Hz, $^1J_{CW} = 140.6$ Hz, $(CO)_4$) (**5**, 17%); 191.68 ppm ($W(CO)_6$, 0.5%); 190.60 ppm ($^1J_{CW} = 136.3$ Hz) (unidentified, but comparable to *trans*-$BrW(CO)_4NO$ at 190.26 ppm ($^1J_{CW} = 133.5$ Hz) at 296 K, 5%)); 128.48, 127.93, 4.037 ppm (minor unidentified CH_3CN peaks). No **4a** or $CH_3CNW(CO)_5$ (CD_2Cl_2, 296 K: 200.44 ($^1J_{CW} = 155.9$ Hz, trans-CO), 196.93 ($^1J_{CW} = 130.2$ Hz, $(CO)_4$), 124.24 4.16 ppm (CH_3CN)) were present. The ^{1}H NMR at the end of acquisition of the 265 K spectrum indicated that **1–4** were present in a ratio of 70:17:7:7. ^{13}C NMR (208 K): 206.06 (br m, $\nu_{1/2} = 6.2$ Hz), 197.10 (br q, $^2J_{CF} = 10.3$ Hz), 129.63, 4.37 ppm (**1**); 204.35, 194.73, 130.60, 4.13, 125.04, 3.66 ppm (**2a**); 214.29 (br s, $\nu_{1/2} = 3.2$ Hz), 126.08, 4.05 ppm (**3**); 193.24 ppm (q, $^2J_{CF} = 12.0$ Hz) (**5**); 191.48 ppm ($W(CO)_6$); 190.53 ppm (unidentified as described above); 128.08, 127.33, 3.89, 3.41 ppm (minor unidentified CH_3CN peaks).

^{19}F NMR Experiment. A sample was prepared as described above with 11.2 mg (0.0307 mmol) of $(AN)W(CO)_5$ (method A), 5.4 mg (0.0462 mmol) of [NO][BF_4], and 2.4 μL (0.0305 mmol) of 1,2-dichloroethane in CD_2Cl_2. Integration of the ^{1}H NMR spectrum gave a 126% yield based on acetonitrile; normalization to 100% gave the following calculated amounts: **1**, 0.0154 mmol; **2a**, 0.002 24 mmol; **3**, 0.001 88 mmol; **4a**, not observed; **5**, 0.004 12 mmol; unreacted $(AN)W(CO)_5$, 0.007 06 mmol; ratio **1**:**2a**:**3**:**4a**:**5**, 65:9:8:0:17; ratio **1**:**3**:**5**, 72:9:19. Integration of the 470.6-MHz ^{19}F NMR recorded at 185 K (Figure 4) gave 79% total $[(\mu\text{-}F)BF_3]^-$ adducts, 18% free $[BF_4]^-$ (−150.3 ppm, br s, $\nu_{1/2} = 50$ Hz), and 3% unidentified $[BF_4]^-$ (−147.3 ppm, br s, $\nu_{1/2} = 30$ Hz). Integration of the doublets due to the terminal fluorine atoms of the ^{11}B isotopomers (the largest signals in the spectrum) gave the ratio **1**:**3**:**5** as 70:11:19, integration of the weaker μ-F quartets gave the ratio **1**:**3**:**5** as 74:13:13, and the total integration of the terminal fluorine atoms to bridging fluorine atoms was 3.08 F to 0.91 F. ^{19}F NMR (185 K): **1**, −153.04 (d, $^2J_{FF} = 95.1$ Hz, ^{10}B), −153.11 (d, $^2J_{FF} = 94.6$ Hz, ^{11}B), −219.39 (q, $^2J_{FF} = 96.0$ Hz) ppm; **3**, −152.96 (d, $^2J_{FF} = 93.5$ Hz, ^{10}B), −153.02 (d, $^2J_{FF} = 94.1$ Hz, ^{11}B), −203.10 (q, $^2J_{FF} = 95.4$ Hz) ppm; **5**, −153.08 (d, $^2J_{FF} = 95.1$ Hz, ^{10}B), −153.14 (d, $^2J_{FF} = 95.5$ Hz, ^{11}B), −238.45 (q, $^2J_{FF} = 95.4$ Hz) ppm. Since the digital resolution was ~2 Hz/point, coupling constants are ~±2 Hz. ^{19}F NMR (220 K): −147.5 (small br s), −150.5 (br s, free $[BF_4]^-$), −153.0 to −153.4 (unresolved $[(\mu\text{-}F)BF_3]^-$, −203.7 (br q, **3**), −219.6 (br q, **1**), −238.6 ppm (br q, **5**). ^{19}F NMR (273 K): −147.8 (small br s), −150.8 (s, $\nu_{1/2} = 150$ Hz) ppm. ^{19}F NMR (298 K): −150.9 ppm (s, $\nu_{1/2} = 400$ Hz).

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