K. Hanson and R. Kerber for helpful discussions. This work was supported by the Division of Chemical Sciences, U.S. Department of Energy, Washington, D.C., under Contract No. DE-AC02-76CH00016.

Registry No. I, 87174-38-7.

Supplementary Material Available: Tables of least-squares planes (Table VI), anisotropic thermal factors of non-hydrogen atoms (Table VII), isotropic thermal factors of hydrogen atoms (Table VIII), and observed and calculated structure factors (Table IX) (27 pages). Ordering information is given on any current masthead page.

Organometallic Nitrosyl Chemistry. 20.[1] (η^5-C_5H_5)W(NO)$_2$BF$_4$, a Versatile Organometallic Electrophile[2]

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Received June 14, 1983

Treatment of a CH_2Cl_2 solution of (η^5-C_5H_5)W(NO)$_2$Cl with an equimolar amount of AgBF$_4$ results in the rapid formation of a precipitate of AgCl and a bright green solution of (η^5-C_5H_5)W(NO)$_2$BF$_4$. This organometallic complex is a thermally unstable, air- and moisture-sensitive species whose characteristic chemistry in CH_2Cl_2 is dominated by its electrophilic nature. Hence, it readily forms adducts of the type [(η^5-C_5H_5)W(NO)$_2$L]BF$_4$ with Lewis bases, L, capable of good σ donation such as PPh$_3$ or P(OPh)$_3$. In an analogous manner, the novel complex [(η^5-C_5H_5)W(NO)$_2$(η^2-C_8H_{14})]BF$_4$ results when (η^5-C_5H_5)W(NO)$_2$BF$_4$ is exposed to an excess of *cis*-cyclooctene. Other olefins, however, either do not react (e.g., allylbenzene) or undergo dimerization (e.g., 1,1-diphenylethene) or isomerization (e.g., 2,3-dimethyl-1-butene), the latter transformations probably occurring via electrophile-induced formation of incipient carbocations. (η^5-C_5H_5)W(NO)$_2$BF$_4$ also reacts with CH_2Cl_2-soluble anionic nucleophiles, X$^-$, to form (η^5-C_5H_5)W(NO)$_2$X (X = H or Br) products. Of greater interest is the fact that the organometallic nitrosyl reactant is sufficiently electrophilic to cleave the M–C linkages in organic derivatives of the main-group elements (i.e., M = B, Al, or Sn) and so produce some new (η^5-C_5H_5)W(NO)$_2$R (R = Et, CH$_2$Ph, or Ph) complexes. This chemistry has also been extended to encompass some of the pentamethylcyclopentadienyl analogues derivable from (η^5-C_5Me_5)W(NO)$_2$BF$_4$. The physical properties of all new compounds prepared are presented and discussed in relation to possible molecular structures.

Introduction

We recently described the preparation and characterization of several salts of the bimetallic cation [(η^5-C_5H_5)$_2$W$_2$(NO)$_4$H]$^+$.[3] The physical and chemical properties of these compounds indicated that the cation could be viewed as a Lewis acid–base adduct. In this view, the formally 18-electron unit (η^5-C_5H_5)W(NO)$_2$H provides a pair of electrons from a filled metal- or ligand-centered orbital to a vacant metal-centered orbital of the formally 16-electron unit (η^5-C_5H_5)W(NO)$_2^+$. Further support for the donor–acceptor character of this interaction was provided by the fact that (η^5-C_5H_5)W(NO)$_2$H also forms adducts with other Lewis acids. On the basis of these studies, it was concluded that (η^5-C_5H_5)W(NO)$_2$H functions as a fairly weak and soft Lewis base.[3] However, little could be said at that time about the acid component of the bimetallic cation. In this paper we now turn our attention to (η^5-C_5H_5)W(NO)$_2^+$. Specifically, we wish to report its independent synthesis and to present its characteristic chemistry that delineates its electrophilic character.

Experimental Section

All reactions and subsequent manipulations involving organometallic reagents were performed under anaerobic and anhydrous conditions. General procedures routinely employed in these laboratories have been described previously.[3] Gas chromatographic analyses were carried out on a Perkin-Elmer Sigma 4B instrument employing a 8 ft × 0.125 in. column packed with 3% OV-17 on Supelcoport.

Generation of a CH_2Cl_2 Solution of (η^5-C_5H_5)W(NO)$_2$BF$_4$. Solid AgBF$_4$ (0.40 g, 2.0 mmol) was added to a green solution of (η^5-C_5H_5)W(NO)$_2$Cl[4] (0.69 g, 2.0 mmol) in CH_2Cl (25 mL) that displayed characteristic nitrosyl absorptions at 1733 and 1650 cm^{-1} in its IR spectrum. The reaction mixture was stirred at room temperature for ~20 min, after which time it consisted of a flocculent white precipitate and a darker green supernatant solution. The final mixture was filtered through a medium-porosity frit to obtain a clear, green solution whose IR spectrum exhibited ν_{NO}'s at 1754 and 1674 cm^{-1}. This solution of (η^5-C_5H_5)W(NO)$_2$BF$_4$ slowly deposited an intractable red-brown solid when stirred at ambient temperature in a prepurified dinitrogen atmosphere, the decomposition being clearly evident after 30 min. The rate of decomposition was markedly enhanced by removal of the solvent in vacuo, an operation which only afforded the red-brown solid. Consequently, the CH_2Cl_2 solutions of (η^5-C_5H_5)W(NO)$_2$BF$_4$ generated according to this procedure were used immediately for the subsequent chemical transformations described below.

Preparation of [(η^5-C_5H_5)W(NO)$_2$L]BF$_4$ (L = PPh$_3$, P(OPh)$_3$, or η^2-C_8H_{14}). The CH_2Cl_2 solution of (η^5-C_5H_5)W(NO)$_2$BF$_4$ was added to a colorless solution of PPh$_3$ (0.53 g, 2.0 mmol) in CH_2Cl_2 (10 mL). The resulting green solution was stirred briefly and was then permitted to stand for ~10 min, whereupon lustrous green platelets began to crystallize. The crystallization was completed by the addition of Et$_2$O (50 mL). The solid was collected by filtration, washed with Et$_2$O (3 × 10 mL), and dried in vacuo (5 × 10^{-3} mm) at room temperature for 0.5 h to obtain 0.94 g (69% yield) of analytically pure [(η^5-C_5H_5)W(NO)$_2$(PPh$_3$)]BF$_4$·$^1/_2$CH$_2$Cl$_2$: IR (CH$_2$Cl$_2$) ν_{NO} 1770 (s), 1694 (vs) cm^{-1}; ^{1}H NMR ((CD$_3$)$_2$CO) δ 7.69 (m, 15 H, C$_6$H$_5$), 6.54 (d, 5 H, C$_5$H$_5$,

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[1] Part 19: Legzdins, P.; Martin, D. T.; Nurse, C. R.; Wassink, B. *Organometallics* 1983, *2*, 1238.

[2] For a preliminary account of this work see: Legzdins, P.; Martin, D. T. "Abstracts of Papers", 185th National Meeting of the American Chemical Society, Seattle, WA, March 1983; American Chemical Society: Washington, DC, 1983; INOR 56.

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$^{3}J_{^{1}H-^{31}P} = 1.2$ Hz), 5.63 (s, 1 H, CH_2Cl_2); mp (in air) 170 °C dec. Anal. Calcd for $C_{23.5}H_{21}N_2BClF_4O_2W$: C, 40.29; H, 3.02; N, 4.00. Found: C, 40.29; H, 3.06; N, 4.04.

A similar sequence of operations involving $P(OPh)_3$ in place of PPh_3 afforded $[(\eta^5\text{-}C_5H_5)W(NO)_2\{P(OPh)_3\}]BF_4$ as a lime-green solid in 82% yield: IR (CH_2Cl_2) ν_{NO} 1786 (s), 1711 (vs) cm^{-1}; ^1H NMR ($(CD_3)_2CO$) δ 7.53 (m, 15 H, C_6H_5), 6.40 (d, 5 H, C_5H_5, $^{3}J_{^{1}H-^{31}P} = 1.0$ Hz); mp (in air) 135 °C dec. Anal. Calcd for $C_{23}H_{20}N_2BF_4O_5PW$: C, 39.13; H, 2.86; N, 3.97. Found: C, 39.26; H, 2.90; N, 3.89.

When a CH_2Cl_2 (5 mL) solution of *cis*-cyclooctene (2.00 mL, 1.69 g, 15.4 mmol) was employed in place of the CH_2Cl_2 solution of PPh_3 in the above procedure, a blue-green solution resulted. The addition of Et_2O (60 mL) to this solution induced the crystallization of 0.37 g (37% yield) of bright green $[(\eta^5\text{-}C_5H_5)W(NO)_2(\eta^2\text{-}C_8H_{14})]BF_4$ which was isolated in the manner described above: IR (CH_2Cl_2) ν_{NO} 1785 (s), 1704 (vs) cm^{-1}; IR (Nujol mull) ν_{NO} 1776 (s), 1674 (vs) cm^{-1}, ν_{BF} 1050 (s, br) cm^{-1}; mp 104 °C dec. Anal. Calcd for $C_{13}H_{19}N_2BF_4O_2W$: C, 30.86; H, 3.78; N, 5.54. Found: C, 30.46; H, 3.64; N, 5.48.

Reaction of $[(\eta^5\text{-}C_5H_5)W(NO)_2(\eta^2\text{-}C_8H_{14})]BF_4$ with $P(OPh)_3$. To a dark green suspension of $[(\eta^5\text{-}C_5H_5)W(NO)_2(\eta^2\text{-}C_8H_{14})]BF_4$ (0.29 g, 0.58 mmol) in CH_2Cl_2 (40 mL) was added neat $P(OPh)_3$ (1.00 mL, 1.18 g, 3.82 mmol). The reaction mixture was stirred for 1 h, whereupon the solid slowly dissolved and the color of the solution changed to light green. Hexanes (40 mL) were then added, and the resulting suspension was filtered through a column of Celite (3 × 5 cm). The filtrate was slowly concentrated under reduced pressure to induce the precipitation of lime-green $[(\eta^5\text{-}C_5H_5)W(NO)_2\{P(OPh)_3\}]BF_4$ (0.28 g, 67% yield) which was identified by its characteristic physical properties (vide supra).

Reaction of $(\eta^5\text{-}C_5H_5)W(NO)_2BF_4$ with Ph_2CCH_2. The CH_2Cl_2 solution of $(\eta^5\text{-}C_5H_5)W(NO)_2BF_4$ was added to a colorless CH_2Cl_2 (10 mL) solution of 1,1-diphenylethene (4.00 mL, 4.12 g, 22.8 mmol). Initially, the reaction mixture became bright blue-green in color, but while it was stirred at room temperature for 18 h, the color lightened and a red-brown precipitate formed. The final mixture was filtered through a 3 × 4 cm column of Florisil supported on a medium-porosity frit. Removal of solvent from the colorless filtrate under reduced pressure left a viscous syrup. Crystallization of this material from light (30–60 °C) petroleum ether afforded a white solid (26% yield based on Ph_2CCH_2) which was identified as 1,1,3-triphenyl-3-methylindan by its characteristic spectral properties:[5] ^1H NMR ($CDCl_3$) δ 7.4–7.0 (m, 19 H, C_6H_5), 3.45, 3.10 (AB q, 2 H, $J_{AB} = 12$ Hz, CH_2), 1.80 (s, 3 H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 150.4, 149.2, 148.7, 148.5, 147.3, 129.1–124.3, 61.22, 60.85, 51.07, 28.79; low resolution mass spectrum (probe temperature 90 °C), *m/z* 360 (P^+), 345 ($[P - Me]^+$), 283 ($[P - Ph]^+$).

Reaction of $(\eta^5\text{-}C_5H_5)W(NO)_2BF_4$ with $H_2CC(CH_3)CH(CH_3)_2$. The CH_2Cl_2 solution of $(\eta^5\text{-}C_5H_5)W(NO)_2BF_4$ was treated with 10.0 mL (6.80 g, 80.8 mmol) of neat 2,3-dimethyl-1-butene. Initially, the reaction mixture acquired a blue-green color which gradually faded over the course of 18 h as a red-brown solid deposited. The final mixture was filtered through a short (3 × 3 cm) column of Florisil to obtain a colorless filtrate. Fractional distillation of the filtrate afforded three fractions: (1) CH_2Cl_2 as the major component of the mixture (bp 40–41 °C), (2) a second, volatile fraction (~2 mL, bp 48 °C), and (3) a small amount of an involatile tar which was not investigated further. ^1H NMR [($CDCl_3$) δ 5.27 (s, 1 H, CH_2Cl_2), 1.64 (s, 22 H, $(CH_3)_2C{=}C(CH_3)_2$)] and gas chromatographic analyses of the second fraction indicated that it was an ~4:1 mixture of 2,3-dimethyl-2-butene and CH_2Cl_2.

Reaction of $(\eta^5\text{-}C_5H_5)W(NO)_2BF_4$ with Ph_3CBr. The CH_2Cl_2 solution of $(\eta^5\text{-}C_5H_5)W(NO)_2BF_4$ was added to a colorless CH_2Cl_2 (10 mL) solution of Ph_3CBr (0.64 g, 2.0 mmol) whereupon the reaction mixture immediately became olive green in color. Solvent was removed in vacuo, the resulting residue was extracted with Et_2O (3 × 40 mL), and the combined extracts were filtered through a Florisil column (3 × 3 cm) to obtain a bright green filtrate. Hexanes (100 mL) were added to the filtrate, and the resulting solution was slowly concentrated under reduced pressure to induce the crystallization of 0.30 g (33% yield) of bright green $(\eta^5\text{-}C_5H_5)W(NO)_2Br$[6] which was collected by filtration: IR (CH_2Cl_2) ν_{NO} 1737 (s), 1656 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.17 (s); low-resolution mass spectrum (probe temperature 80 °C), *m/z* 388, 390 (P^+), 358, 360 ($[P - NO]^+$). Anal. Calcd for $C_5H_5N_2BrO_2W$: C, 15.44; H, 1.30; N, 7.20. Found: C, 15.44; H, 1.28; N, 7.12.

Reaction of $(\eta^5\text{-}C_5H_5)W(NO)_2BF_4$ with [PPN]Br.[7] The CH_2Cl_2 solution of $(\eta^5\text{-}C_5H_5)W(NO)_2BF_4$ was added to a colorless solution of [PPN]Br (1.25 g, 2.0 mmol) in CH_2Cl_2 (5 mL). The resulting green solution was stirred briefly at room temperature before being treated with Et_2O (75 mL). This operation resulted in the precipitation of most (i.e., 1.02 g, 1.62 mmol) of the $[PPN]BF_4$ byproduct as a white solid which was removed by filtration. Solvent was removed from the filtrate in vacuo, and the remaining green solid was redissolved in a minimum amount of CH_2Cl_2 (~5 mL). This solution was transferred by syringe to the top of a Florisil column (3 × 4 cm) made up in CH_2Cl_2. Elution of the column with CH_2Cl_2 resulted in the development of a single, green band which was collected. The eluate was concentrated under reduced pressure to ~20 mL before being diluted with hexanes (40 mL). Further concentration of this solution led to the crystallization of $(\eta^5\text{-}C_5H_5)W(NO)_2Br$ (0.51 g, 58% yield) as a bright green solid (vide supra).

Reaction of $(\eta^5\text{-}C_5H_5)W(NO)_2BF_4$ with $[PPN]BH_4$. The CH_2Cl_2 solution of $(\eta^5\text{-}C_5H_5)W(NO)_2BF_4$ was added to a colorless solution of $[PPN]BH_4$[8] (1.16 g, 2.00 mmol) in CH_2Cl_2 (5 mL) at −78 °C. The resulting green solution was permitted to warm to room temperature while being stirred. Volatile components were removed from the final mixture in vacuo to leave a solid green residue which was extracted with Et_2O (3 × 20 mL). The extracts were taken to dryness under reduced pressure to obtain 0.35 g (56% yield) of a green solid which was identified as $(\eta^5\text{-}C_5H_5)W(NO)_2H$ by comparison with an authentic sample:[9] IR (CH_2Cl_2) ν_{NO} 1718 (s), 1632 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.00 (s, 5 H, C_5H_5), 2.07 (s, 1 H, WH).

Reaction of $(\eta^5\text{-}C_5H_5)W(NO)_2BF_4$ with $Na[BPh_4]$. The CH_2Cl_2 solution of $(\eta^5\text{-}C_5H_5)W(NO)_2BF_4$ was added to a suspension of $Na[BPh_4]$ (0.69 g, 2.0 mmol) in CH_2Cl_2 (35 mL). The resulting mixture was stirred at room temperature for ~1 h, during which time it developed a red-brown coloration. The final mixture was filtered through a short (3 × 6 cm) column of alumina (Woelm neutral, activity 1) supported on a medium-porosity frit. The bright green filtrate was taken to dryness in vacuo to obtain 0.38 g (48% yield) of a bright green solid which was readily identified as $(\eta^5\text{-}C_5H_5)W(NO)_2Ph$ by its characteristic spectroscopic properties:[10] IR (CH_2Cl_2) ν_{NO} 1720 (s), 1634 (vs) cm^{-1}; ^1H NMR (C_6D_6) δ 7.42 (m, 5 H, C_6H_5), 5.06 (s, 5 H, C_5H_5); low-resolution mass spectrum (probe temperature 80 °C), *m/z* 386 (P^+), 356 ($[P - NO]^+$), 326 ($[P - 2NO]^+$).

Reaction of $(\eta^5\text{-}C_5H_5)W(NO)_2BF_4$ with Et_3Al. The CH_2Cl_2 solution of $(\eta^5\text{-}C_5H_5)W(NO)_2BF_4$ was added to 1 mL of a 25% by weight, colorless solution of Et_3Al in toluene maintained at −78 °C. Immediately, the reaction mixture became red-brown in color. It was stirred at −78 °C for 5 min before being allowed to warm to room temperature. The final mixture was then filtered through a column (3 × 6 cm) of alumina (Woelm neutral, activity 1) supported on a medium-porosity frit to obtain a bright green filtrate. Removal of solvent from this filtrate under reduced pressure produced a viscous green oil. Sublimation of this oil (40 °C, 5×10^{-3} mm) onto a water-cooled probe afforded 0.11 g (16% yield) of $(\eta^5\text{-}C_5H_5)W(NO)_2Et$ as an analytically pure, crystalline, green solid. IR (CH_2Cl_2) ν_{NO} 1707 (s), 1619 (vs) cm^{-1}; ^1H NMR (C_6D_6) δ 4.98 (s, 5 H, C_5H_5), 1.96 (m, 5 H, CH_2CH_3); low-resolution mass spectrum (probe temperature 55 °C), *m/z* 338 (P^+), 308 ($[P - NO]^+$), 278 ($[P - 2NO]^+$).

Anal. Calcd for $C_7H_{10}N_2O_2W$: C, 24.87; H, 2.98; N, 8.29. Found: C, 25.05; H, 2.97; N, 8.31.

Preparation of $(PhCH_2)_4Sn$. A solution of benzyl chloride (1.73 mL, 2.53 g, 20.0 mmol) in THF (25 mL) was added dropwise to a mixture of magnesium turnings (1.00 g, 41.1 mmol) and THF

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(100 mL). The final mixture was stirred for 2 h without being permitted to warm above room temperature. At the end of this time, it was treated with a THF (15 mL) solution of $(PhCH_2)_3SnCl$[11] (4.27 g, 10.0 mmol), and the resulting mixture was stirred at reflux for 18 h before being hydrolyzed with cold, deionized H_2O (50 mL). The organic phase was separated and dried over anhydrous $CaCl_2$ before solvent was removed from it in vacuo. The remaining colorless syrup was crystallized from light (30–60 °C) petroleum ether at −78 °C to obtain pure $(PhCH_2)_4Sn$ (2.33 g, 48% yield) as a white solid: ^1H NMR ($CDCl_3$) δ 7.24–7.05 (m, 20 H, C_6H_5), 2.21 (s, 8 H, CH_2); mp 42 °C.

Anal. Calcd for $C_{28}H_{28}Sn$: C, 69.60; H, 5.84. Found: C, 69.75; H, 5.91.

Reaction of $(\eta^5\text{-}C_5H_5)W(NO)_2BF_4$ with $(PhCH_2)_4Sn$. The CH_2Cl_2 solution of $(\eta^5\text{-}C_5H_5)W(NO)_2BF_4$ was added to a colorless solution of $(PhCH_2)_4Sn$ (0.96 g, 2.0 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred at room temperature for ~90 min during which time a brown precipitate formed, and the color of the supernatant solution became olive green. The final mixture was filtered through a 3 × 4 cm column of Florisil to obtain an olive green filtrate. The addition of hexanes (50 mL) to the filtrate and slow concentration of the resulting solution under reduced pressure induced the crystallization of 0.14 g (18% yield) of $(\eta^5\text{-}C_5H_5)W(NO)_2CH_2Ph$ as a green solid which was collected by filtration: IR (CH_2Cl_2) ν_{NO} 1714 (s), 1626 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.30–7.07 (m, 5 H, C_6H_5), 5.81 (s, 5 H, C_5H_5), 3.17 (s, 2 H, CH_2); low-resolution mass spectrum (probe temperature 75 °C), m/z 400 (P^+), 370 ($[P-NO]^+$), 340 ($[P-2NO]^+$), 91 ($C_7H_7^+$). Anal. Calcd for $C_{12}H_{12}N_2O_2W$: C, 36.02; H, 3.02; N, 7.00. Found: C, 36.68; H, 3.11; N, 6.75.

Preparation of $(\eta^5\text{-}C_5H_5)W(NO)_2OSO_2C_6H_4CH_3$. Solid $(\eta^5\text{-}C_5H_5)W(NO)_2Cl$ (0.69 g, 2.0 mmol) was added to a slurry of silver *p*-toluenesulfonate (0.56 g, 2.0 mmol) in CH_2Cl_2 (25 mL). The reaction mixture was stirred for 3 h during which time its physical appearance did not change. The final mixture was filtered through a short column of Celite (3 × 5 cm) supported on a medium-porosity frit. Concentration of the filtrate in vacuo resulted in the formation of a green solid which was collected by filtration, washed with hexanes (3 × 10 mL), and dried (5 × 10^{-3} mm). The solid was identified as $(\eta^5\text{-}C_5H_5)W(NO)_2OSO_2C_6H_4CH_3$ (0.67 g, 70% yield) by comparison of its IR, ^1H NMR, and mass spectrum with those displayed by an authentic sample prepared previously:[9] IR (CH_2Cl_2) ν_{NO} 1737 (s), 1650 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.41 (m, 4 H, $C_6H_4CH_3$), 6.15 (s, 5 H, C_5H_5), 2.70 (s, 3 H, $C_6H_4CH_3$); low-resolution mass spectrum (probe temperature 165 °C), m/z 480 (P^+).

Preparation of $(\eta^5\text{-}C_5Me_5)W(NO)_2Cl$. To a rapidly stirred, orange solution of $(\eta^5\text{-}C_5Me_5)W(CO)_2(NO)$[12] (4.68 g, 11.6 mmol) in CH_2Cl_2 (75 mL) at −78 °C was added dropwise a CH_2Cl_2 solution of ClNO (containing 2.0 g of ClNO in 30 mL of CH_2Cl_2).[13] Gas evolution occurred, and the reaction mixtured darkened in color. The progress of the reaction was monitored by IR spectroscopy, and the ClNO solution was added until the carbonyl absorptions due to the organometallic reactant had disappeared. The final green reaction mixture was then permitted to warm to room temperature before being concentrated in vacuo to ~10 mL. This solution was transferred by syringe onto the top of a 3 × 5 cm column of Florisil made up in CH_2Cl_2. Elution of the column with CH_2Cl_2 produced a bright green band which was collected. Addition of hexanes (100 mL) to the eluate, followed by slow concentration of the resulting solution under reduced pressure, afforded 2.48 g (52% yield) of the green, crystalline product which was collected by filtration: IR (CH_2Cl_2): ν_{NO} 1705 (s), 1625 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.03 (s); low resolution mass spectrum (probe temperature 95 °C), m/z 414 (P^+); mp (in air) 188 °C. Anal. Calcd for $C_{10}H_{15}N_2ClO_2W$: C, 28.97; H, 3.64; N, 6.76. Found: C, 28.97; H, 3.70; N, 6.68.

Preparation of $(\eta^5\text{-}C_5Me_5)W(NO)_2H$. A green toluene (25 mL) solution containing $(\eta^5\text{-}C_5Me_5)W(NO)_2Cl$ (0.73 g, 1.76 mmole at −78 °C was treated dropwise with a colorless toluene solution of $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ (0.6 mL of a 70% toluene solution diluted to 10 mL). No change in the appearance of the reaction mixture was immediately apparent. After all the aluminum reagent had been added, the mixture was stirred for 30 min to ensure complete reaction. At the end of that time, and without being warmed to room temperature, the final mixture was filtered quickly through a column of Florisil (3 × 5 cm) supported on a medium-porosity frit. The filtrate was taken to dryness in vacuo, and the resulting residue was crystallized from hexanes to obtain $(\eta^5\text{-}C_5Me_5)W(NO)_2H$ as well-formed, green crystals (0.42 g, 63% yield): IR (hexanes) ν_{W-H} 1894 (w) cm^{-1}, ν_{NO} 1704 (s), 1626 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.17 (s, 1 H, WH), 2.17 (s, 15 H, $C_5(CH_3)_5$); low-resolution mass spectrum (probe temperature 35 °C) m/z 380 (P^+); mp 77 °C dec. Anal. Calcd for $C_{10}H_{16}N_2O_2W$: C, 31.60; H, 4.24; N, 7.39. Found: C, 31.36; H, 4.27; N, 7.24.

Preparation of $[(\eta^5\text{-}C_5Me_5)W(NO)_2(PPh_3)]BF_4$. Method A. Solid $AgBF_4$ (0.20 g, 1.0 mmol) was added to a stirred green solution of $(\eta^5\text{-}C_5Me_5)W(NO)_2Cl$ (0.42 g, 1.0 mmol) in CH_2Cl_2 (20 mL). A flocculent white precipitate formed while the reaction mixture was stirred for 30 min. The final mixture was filtered into a CH_2Cl_2 (5 mL) solution of PPh_3 (0.27 g, 1.0 mmol) to obtain a green solution. Hexanes (25 mL) were added, and the solution was slowly concentrated under reduced pressure to induce the crystallization of $[(\eta^5\text{-}C_5Me_5)W(NO)_2(PPh_3)]BF_4$ as a green solid (0.46 g, 63% yield).

Method B. To a stirred green solution of $(\eta^5\text{-}C_5Me_5)W(NO)_2H$ (0.38 g, 1.0 mmol) in CH_2Cl_2 (20 mL) was added solid Ph_3CBF_4 (0.33 g, 1.0 mmol). The resulting solution was stirred for ~15 min, whereupon PPh_3 (0.27 g, 1.0 mmol) was added. The subsequent addition of hexanes (15 mL) and slow concentration of the final solution in vacuo led to the precipitation of 0.61 g (84% yield) of the product complex: IR (CH_2Cl_2) ν_{NO} 1744 (s), 1673 (vs) cm^{-1}; ^1H NMR ($(CD_3)_2CO$) δ 2.05 (d, 15 H, $C_5(CH_3)_5$, $^4J_{^1H-^{31}P}$ = 0.5 Hz), 7.72 (m, 15 H, C_6H_5); mp (in air) 144 °C dec.

Anal. Calcd for $C_{28}H_{30}N_2BF_4O_2PW$: C, 46.18; H, 4.15; N, 3.85. Found: C, 45.73; H, 4.21; N, 3.77.

Preparation of $(\eta^5\text{-}C_5Me_5)W(NO)_2Et$. A solution of $(\eta^5\text{-}C_5Me_5)W(NO)_2BF_4$ was generated from $AgBF_4$ (0.20 g, 1.0 mmol) and $(\eta^5\text{-}C_5Me_5)W(NO)_2Cl$ (0.41 g, 1.0 mmol) in CH_2Cl_2 (10 mL) (vide supra). This solution was added to a colorless solution of Et_3Al (0.11 g, 1.0 mmol) in toluene (2 mL) at −78 °C. This operation resulted in the formation of a dark red solution which, upon warming to room temperature, gradually acquired a green-brown coloration. The final mixture was filtered through an alumina column (3 × 6 cm, Woelm neutral, activity 1), and the green filtrate was taken to dryness in vacuo. Sublimation of the oily residue (75 °C, 5 × 10^{-3} mm) onto a water-cooled probe afforded the product complex as a green solid (0.02 g, 5% yield): IR (hexanes) ν_{NO} 1685 (s), 1606 (vs) cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.95 (s, 15 H, $C_5(CH_3)_5$), 1.96 (q, 2 H, CH_2CH_3, J = 7.3 Hz), 1.27 (t, 3 H, CH_2CH_3); low-resolution mass spectrum (probe temperature 55 °C) m/z 408 (P^+). Anal. Calcd for $C_{12}H_{20}N_2O_2W$: C, 35.31; H, 4.94; N, 6.86. Found: C, 35.31; H, 5.02; N, 6.68.

Results and Discussion

Preparation of $(\eta^5\text{-}C_5H_5)W(NO)_2BF_4$. When a dichloromethane solution of $(\eta^5\text{-}C_5H_5)W(NO)_2Cl$ is treated with an equimolar amount of $AgBF_4$, a precipitate of AgCl rapidly forms. The chloride abstraction reaction which occurs, i.e., eq 1, is complete in 20 min at room temperature

$$(\eta^5\text{-}C_5H_5)W(NO)_2Cl + AgBF_4 \xrightarrow{CH_2Cl_2} (\eta^5\text{-}C_5H_5)W(NO)_2BF_4 + AgCl\downarrow \quad (1)$$

as monitored by solution IR spectroscopy. The nitrosyl stretching absorptions at 1733 (s) and 1650 (vs) cm^{-1} characteristic of the organometallic reactant gradually diminish in intensity and are eventually replaced by new bands at 1754 (s) and 1674 (vs) cm^{-1} which can be assigned as the ν_{NO}'s of $(\eta^5\text{-}C_5H_5)W(NO)_2BF_4$. [When reaction 1 is effected in CD_2Cl_2, its progress can be easily monitored by ^1H NMR spectroscopy, the cyclopentadienyl proton resonance of $(\eta^5\text{-}C_5H_5)W(NO)_2Cl$ at δ 6.16 being replaced cleanly by a new singlet at slightly lower field (δ 6.27).]

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[11] Sisido, K.; Takeda, S.; Kinugawa, Z. *J. Am. Chem. Soc.* **1961**, *83*, 538.

[12] Malito, J. T.; Shakir, R.; Atwood, J. L. *J. Chem. Soc., Dalton Trans.* **1980**, 1253.

[13] For a description of the handling of ClNO solutions see ref 4.

The relatively facile manner in which this transformation proceeds is noteworthy. The related reactions between $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{X}$ (X = Br[14] or I[15]) and Ag(I) salts are slower and proceed in a stepwise fashion, e.g., eq 2; the

$$(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{I} + 0.5\text{AgBF}_4 \xrightarrow{\text{CH}_2\text{Cl}_2} 0.5[\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\}_2\text{I}]\text{BF}_4 + 0.5\text{AgI} \xrightarrow[0.5\text{AgBF}_4]{\text{CH}_2\text{Cl}_2} (\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{BF}_4 + 0.5\text{AgI} \quad (2)$$

second step not occurring until the first is complete. The isoelectronic chromium nitrosyl analogue of the intermediate halide-bridged, bimetallic cations has also recently been synthesized in a similar manner,[16] i.e., eq 3. However, spectroscopic monitoring of the progress of reaction 1 provides no evidence for even the transient formation of $[\{(\eta^5\text{-C}_5\text{H}_5)\text{W(NO)}_2\}_2\text{Cl}]\text{BF}_4$ during this conversion.

$$(\eta^5\text{-C}_5\text{H}_5)\text{Cr(NO)}_2\text{Cl} + [(\eta^5\text{-C}_5\text{H}_5)\text{Cr(NO)}_2\text{SO}_2]\text{AsF}_6 \xrightarrow{-\text{SO}_2} [\{(\eta^5\text{-C}_5\text{H}_5)\text{Cr(NO)}_2\}_2\text{Cl}]\text{AsF}_6 \quad (3)$$

Removal by filtration of the AgCl byproduct formed in reaction 1 produces a bright green CH_2Cl_2 solution of the desired organometallic product that fumes profusely when exposed to the atmosphere. Regrettably, this solution is also thermally unstable, depositing only insoluble decomposition products when maintained under an atmosphere of prepurified dinitrogen at room temperature. Consequently, we have as yet been unable to isolate $(\eta^5\text{-C}_5\text{H}_5)\text{W(NO)}_2\text{BF}_4$ in the solid state and to determine its exact identity. Nevertheless, given what is currently known about such related complexes as $(\eta^5\text{-C}_5\text{H}_5)\text{Cr(NO)}_2\text{FPF}_5$,[17] $(\eta^5\text{-C}_5\text{H}_5)\text{W(CO)}_3\text{Y}$ (Y = FBF_3 or FPF_5),[18] and $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{FBF}_3$,[15] it is likely that the complex possesses the BF_4^- anion ligated weakly in a monodentate fashion. Alternatively, $(\eta^5\text{-C}_5\text{H}_5)\text{W(NO)}_2\text{BF}_4$ may exist in CH_2Cl_2 as discrete ion pairs with the coordinatively unsaturated organometallic cation possibly incorporating a molecule of solvent into the metal's coordination sphere. In any event, the characteristic chemistry of the compound in CH_2Cl_2 is dominated by its electrophilic nature, and during its reactions with various nucleophiles it behaves as though it were the formally 16-electron $[(\eta^5\text{-C}_5\text{H}_5)\text{W(NO)}_2]^+$.

The Characteristic Chemistry of $(\eta^5\text{-C}_5\text{H}_5)\text{W(NO)}_2\text{BF}_2$. (a) Reactions with Strong Lewis Bases. Not surprisingly, $(\eta^5\text{-C}_5\text{H}_5)\text{W(NO)}_2\text{BF}_4$ readily forms adducts with good donor ligands, i.e., eq 4, the resulting salts

$$(\eta^5\text{-C}_5\text{H}_5)\text{W(NO)}_2\text{BF}_4 + \text{L} \xrightarrow{\text{CH}_2\text{Cl}_2} [(\eta^5\text{-C}_5\text{H}_5)\text{W(NO)}_2\text{L}]\text{BF}_4 \quad (4)$$

$$\text{L} = \text{PPh}_3 \text{ or } \text{P(OPh)}_3$$

being isolable in good yields. The organometallic cations obtained from reaction 4 have been prepared previously as their PF_6^- salts by substitution of the carbonyl ligand in $(\eta^5\text{-C}_5\text{H}_5)\text{W(NO)}_2\text{(CO)}]\text{PF}_6$.[6] The physical properties of the BF_4^- salts are generally indistinguishable from those of their PF_6^- analogues. Thus, IR spectra of $[(\eta^5\text{-C}_5\text{H}_5)\text{W(NO)}_2(\text{PPh}_3)]\text{BF}_4$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{W(NO)}_2\{\text{P(OPh)}_3\}]\text{BF}_4$ in CH_2Cl_2 display strong nitrosyl absorptions at 1770, 1694 and 1786, 1711 cm^{-1}, respectively, which are some 40–60 cm^{-1} higher in energy than those exhibited by $(\eta^5\text{-C}_5\text{H}_5)\text{W(NO)}_2\text{Cl}$ in the same solvent. More significantly, they are also some 20–30 cm^{-1} higher in energy than the ν_{NO}'s of $(\eta^5\text{-C}_5\text{H}_5)\text{W(NO)}_2\text{BF}_4$. This fact is not consistent with the latter complex undergoing dissociation in CH_2Cl_2 to form discrete, or even solvated, $[(\eta^5\text{-C}_5\text{H}_5)\text{W(NO)}_2]^+$ cations (vide supra). Such an inference is based, of course, solely on the anticipated amount of electron density available on the tungsten center for back-donation to the NO ligands in the various complexes and takes no account of any structural differences between them. The ^1H NMR spectra of the BF_4^- complexes in acetone-d_6 display the expected features.

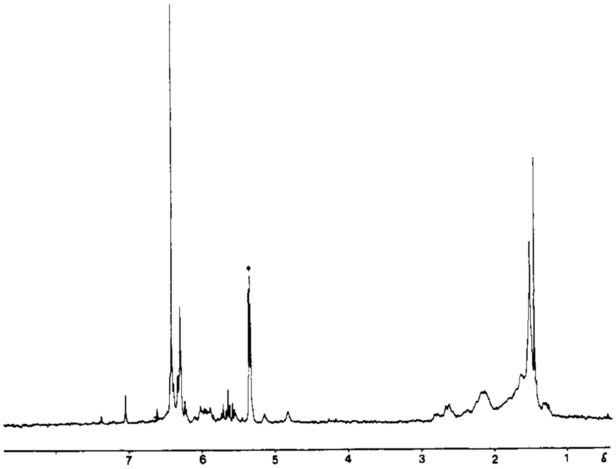
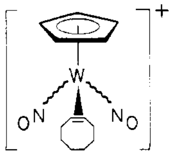


Figure 1. The 80-MHz ^1H FT NMR spectrum of $[(\eta^5\text{-C}_5\text{H}_5)\text{W(NO)}_2(\eta^2\text{-C}_8\text{H}_{14})]\text{BF}_4$ in CD_2Cl_2*.

(b) Reactions with Olefins. The introduction of an excess of *cis*-cyclooctene into a CH_2Cl_2 solution of $(\eta^5\text{-C}_5\text{H}_5)\text{W(NO)}_2\text{BF}_4$ results in the establishment of the equilibrium (5) when can be disturbed by the addition of

$$(\eta^5\text{-C}_5\text{H}_5)\text{W(NO)}_2\text{BF}_4 + \text{C}_8\text{H}_{14} \xrightleftharpoons{\text{CH}_2\text{Cl}_2} [(\eta^5\text{-C}_5\text{H}_5)\text{W(NO)}_2(\eta^2\text{-C}_8\text{H}_{14})]\text{BF}_4 \quad (5)$$

Et_2O to induce the precipitation of the new alkene dinitrosyl product in 37% yield. The product complex is a bright green, crystalline solid which is thermally stable but, unlike the phosphine and phosphite complexes described in the preceding section, must be handled exclusively in an atmosphere completely free of moisture and oxygen. It is insoluble in nonpolar organic solvents such as hexanes or benzene but is only sparingly soluble in dichloromethane. The spectral properties of $[(\eta^5\text{-C}_5\text{H}_5)\text{W(NO)}_2(\eta^2\text{-C}_8\text{H}_{14})]\text{BF}_4$ are consistent with the organometallic cation having the "piano stool" molecular structure.



Thus, an IR spectrum of the complex as a Nujol mull exhibits two strong absorptions at 1776 and 1674 cm^{-1} attributable to the terminal nitrosyl ligands. Furthermore, there is a broad, strong band at 1050 cm^{-1} characteristic of a tetrahedral BF_4^- anion.

The ^1H NMR spectrum of $[(\eta^5\text{-C}_5\text{H}_5)\text{W(NO)}_2(\eta^2\text{-C}_8\text{H}_{14})]\text{BF}_4$ in CD_2Cl_2 (Figure 1) confirms the equilibrium nature of reaction 5 and establishes a value of ~2 for the equilibrium constant at ambient temperature. The two cyclopentadienyl proton resonances at δ 6.39 and 6.27 of relative intensity ~2:1 can be assigned to $[(\eta^5\text{-C}_5\text{H}_5)\text{W}$-

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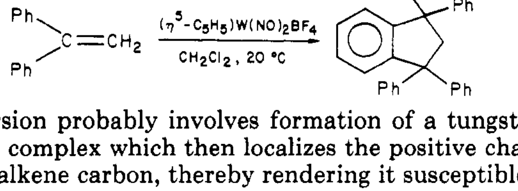
$(NO)_2(\eta^2\text{-}C_8H_{14})]BF_4$ and $(\eta^5\text{-}C_5H_5)W(NO)_2BF_4$, respectively. The multiplet at δ 5.65 is due to the vinyl protons of free cyclooctene and has an integrated area which is $^2/_5$ that of the signal at δ 6.27. By analogy, the broad, unresolved multiplet at δ 5.93 which is $^2/_5$ as intense as the resonance at δ 6.39 can be assigned to the vinyl protons of coordinated C_8H_{14}. [The remaining signals between δ 2.61 and 1.41 are attributable to the ring methylene protons of both free and complexed cyclooctene.] This shift of the signals due to the vinyl protons to lower field upon complexation of C_8H_{14} to $(\eta^5\text{-}C_5H_5)W(NO)_2BF_4$ is exactly opposite to what is customarily observed when olefins coordinate to transition metals[19] (cf. $(\eta^5\text{-}C_5H_5)Cr(CO)(NO)(\eta^2\text{-}C_8H_{14})$[20]). Within the confines of the generally accepted Dewar–Chatt–Duncanson model for olefin–metal bonding,[21] it is tempting to interpret this deshielding as indicating diminished π back-bonding from W to the $\eta^2\text{-}C_8H_{14}$ ligand. This view that $C_8H_{14}{\rightarrow}W$ σ bonding is the principal contributor to the olefin–metal bond in $[(\eta^5\text{-}C_5H_5)W(NO)_2(\eta^2\text{-}C_8H_{14})]BF_4$ is supported by the fact that this linkage is relatively weak, being readily cleaved by Lewis bases capable of better σ donation than cyclooctene. Thus, when a small amount of acetone-d_6 is added to the CD_2Cl_2 solution of the complex, the only ^1H NMR signals that persist are those due to free C_8H_{14} and a singlet at δ 6.47 probably due to the C_5H_5 protons of $[(\eta^5\text{-}C_5H_5)W(NO)_2\{(CD_3)_2CO\}]BF_4$. In a similar manner, the conversion shown in eq 6 affords the familiar phosphite complex in good yield.

$$[(\eta^5\text{-}C_5H_5)W(NO)_2(\eta^2\text{-}C_8H_{14})]BF_4 + P(OPh)_3 \xrightarrow{CH_2Cl_2} [(\eta^5\text{-}C_5H_5)W(NO)_2\{P(OPh)_3\}]BF_4 + C_8H_{14} \quad (6)$$

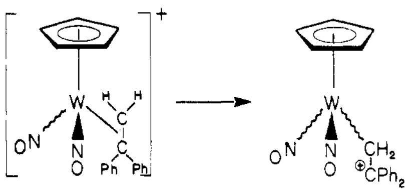
Mindful of the various factors which influence the stability of other transition-metal-alkene complexes,[22] we originally anticipated that it would be possible to synthesize more stable $[(\eta^5\text{-}C_5H_5)W(NO)_2(\eta^2\text{-olefin})]BF_4$ complexes by simply replacing C_8H_{14} in reaction 5 with olefins such as ethene, propene, *cis*-2-butene, etc. Unfortunately, such has not proven to be the case. Even though the CH_2Cl_2 solutions of $(\eta^5\text{-}C_5H_5)W(NO)_2BF_4$ do develop a blue-green coloration initially when treated with olefinic substrates, the rate of decomposition of the organometallic reactant is not significantly diminished (vide supra). Consequently, we then turned our attention to ascertaining the eventual fate of the organic substrates.

Some olefins, such as allylbenzene, simply do not react with $(\eta^5\text{-}C_5H_5)W(NO)_2BF_4$ and can be recovered unchanged from the final reaction mixture. Others, however, do undergo interesting transformations. For example, 1,1-diphenylethene undergoes a clean (but not efficient) "dimerization", i.e., eq 7. The initiation step of this



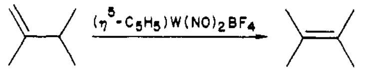
(7)

conversion probably involves formation of a tungsten–alkene complex which then localizes the positive charge on an alkene carbon, thereby rendering it susceptible to nucleophilic attack by another molecule of the olefin, i.e., eq 8. 2,3-Dimethyl-1-butene, on the other hand, undergoes



(8)

a rapid double-bond isomerization, i.e., eq 9, a fact that again provides evidence for the ability of $(\eta^5\text{-}C_5H_5)W(NO)_2BF_4$ to generate incipient carbocations. In this



(9)

connection, it can be noted that the electrophilicity of the related $[W(NO)_2(CH_3CN)_4]^{2+}$ cation (from which $(\eta^5\text{-}C_5H_5)W(NO)_2{}^+$ may be considered, at least in a formal sense, to be derived) has recently been exploited by Sen and Thomas[5] during catalysis of similar polymerization, oligomerization, and rearrangement reactions of various olefins.

It thus appears that in order to form an adduct with $(\eta^5\text{-}C_5H_5)W(NO)_2BF_4$ via reaction 5, an olefin must simultaneously satisfy two criteria, namely, (1) it must be capable of functioning as a reasonbly strong σ-electron donor and (2) it must not readily undergo electrophile-induced transformations. The only olefin that has met these criteria to date is cyclooctene. Interestingly, the recently described[23] $[(\eta^5\text{-}C_5H_5)Co(NO)(\eta^2\text{-}C_8H_{14})]PF_6$ is also the only olefin-containing complex in its class of compounds.

(c) Reactions with Anionic Nucleophiles. If reaction 1 is attempted with the silver(I) salt of a coordinating anion such as *p*-toluenesulfonate, the anion becomes firmly bound to the tungsten center, i.e., eq 10. [We have pre-

$$(\eta^5\text{-}C_5H_5)W(NO)_2Cl + AgOSO_2C_6H_4CH_3 \xrightarrow{CH_2Cl_2} (\eta^5\text{-}C_5H_5)W(NO)_2OSO_2C_6H_4CH_3 + AgCl\downarrow \quad (10)$$

viously obtained the organometallic product of reaction 10 by treating $(\eta^5\text{-}C_5H_5)W(NO)_2H$ with a stoichiometric amount of anhydrous *p*-toluenesulfonic acid.[9]] This binding of the anion by the metal center suggested to us that $(\eta^5\text{-}C_5H_5)W(NO)_2BF_4$ would be prone to nucleophilic attack by various anions. However, in order to exploit this reactivity successfully, it is mandatory that the desired reactions proceed promptly in CH_2Cl_2 so that the integrity of the nitrosyl-containing electrophile is maintained (vide supra). This practical limitation thus excludes the use of anionic reagents that either react readily with CH_2Cl_2 or have insufficient solubility in this solvent to permit rapid reaction with $(\eta^5\text{-}C_5H_5)W(NO)_2BF_4$. Fortunately, $[PPN]^+$ salts[7] are not hampered by either restriction.

As an unremarkable example of this type of chemistry, we have found that $(\eta^5\text{-}C_5H_5)W(NO)_2BF_4$ reacts cleanly with [PPN]Br to yield the well-known $(\eta^5\text{-}C_5H_5)W(NO)_2Br$ complex, i.e., eq 11. More significantly, treatment of

$$(\eta^5\text{-}C_5H_5)W(NO)_2BF_4 + [PPN]Br \xrightarrow{CH_2Cl_2} (\eta^5\text{-}C_5H_5)W(NO)_2Br + [PPN]BF_4 \quad (11)$$

$(\eta^5\text{-}C_5H_5)W(NO)_2BF_4$ with $[PPN]BH_4$ produces the corresponding metal hydride, i.e., eq 12. The isolated yield

$$(\eta^5\text{-}C_5H_5)W(NO)_2BF_4 + [PPN]BH_4 \xrightarrow{CH_2Cl_2} (\eta^5\text{-}C_5H_5)W(NO)_2H + [PPN]BF_4 + BH_3 \quad (12)$$

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[19] (a) Kochi, J. K.; Salomon, R. G. *J. Organomet. Chem.* **1972**, *43*, C7. (b) Kochi, J. K.; Salomon, R. G. *Ibid.* **1974**, *64*, 135.

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[23] Connelly, N. G.; Payne, J. D.; Geiger, W. E. *J. Chem. Soc., Dalton Trans.* **1983**, 295.

of (η^5-C_5H_5)W(NO)$_2$H from this reaction (56%) compares favorably with that which we previously reported from the reaction of Na[$AlH_2(OCH_2CH_2OCH_3)_2$] with (η^5-C_5H_5)W(NO)$_2$Cl (i.e., 61%) and is considerably better than the yields obtained from the reactions of $NaBH_4$ (in THF) with (η^5-C_5H_5)W(NO)$_2$Cl or [(η^5-C_5H_5)W(NO)$_2$(CO)]PF_6 (13% and 23%, respectively).[9] In fact, reaction 12 represents the cleanest and most convenient method for the synthesis of the hydrido nitrosyl complex.

The affinity of (η^5-C_5H_5)W(NO)$_2BF_4$ for halide ion demonstrated by reaction 11 is also evident during its reaction with bromotriphenylmethane, i.e., eq 13. Hence,

$$(\eta^5\text{-}C_5H_5)W(NO)_2BF_4 + Ph_3CBr \xrightarrow{CH_2Cl_2} (\eta^5\text{-}C_5H_5)W(NO)_2Br + [Ph_3C]BF_4 \quad (13)$$

as far as Br^- is concerned, (η^5-C_5H_5)W(NO)$_2^+$ is a more potent electrophile than Ph_3C^+. In contrast, when H^- is the nucleophile involved, the reverse of reaction 13 occurs.[3] This pronounced affinity of (η^5-C_5H_5)W(NO)$_2BF_4$ for halide ions may account for the fact that [{(η^5-C_5H_5)W(NO)$_2$}$_2$Cl]BF_4 is not detectable as an intermediate during the progress of reaction 1 (vide supra).

Of greater interest to us than these new synthetic routes leading to the (η^5-C_5H_5)W(NO)$_2$X (X = H or Br) compounds was the possibility that (η^5-C_5H_5)W(NO)$_2BF_4$ might be utilized to effect the preparation of novel, neutral alkyl or aryl derivatives of the type (η^5-C_5H_5)W(NO)$_2$R (R = alkyl or aryl). Our previous studies directed at the synthesis of these complexes[10] had established the following features: (1) metathesis reactions between (η^5-C_5H_5)W(NO)$_2$Cl and various RLi and RMgX reagents fail to yield even spectroscopically detectable quantities of (η^5-C_5H_5)W(NO)$_2$R. Evidently this is so because the organolithium and Grignard reagents are too potent to effect the selective nucleophilic displacement of Cl^- and attack other functional groups as well.[24] (2) When the gentler and more selective R_3Al compounds are employed as the alkylating or arylating agents in place of RLi or RMgX, the transformation shown in eq 14 is successful when R

$$(\eta^5\text{-}C_5H_5)W(NO)_2Cl + R\text{-}Al< \xrightarrow{\text{benzene}} (\eta^5\text{-}C_5H_5)W(NO)_2R + Cl\text{-}Al< \quad (14)$$

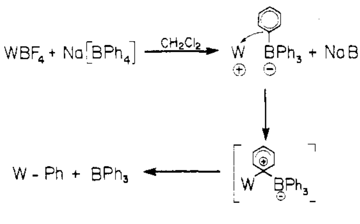
= Me or Ph. However, unlike for the congeneric Cr and Mo complexes, reaction 14 is not generally applicable for the synthesis of a variety of (η^5-C_5H_5)W(NO)$_2$R complexes. This fact is probably a reflection of the greater strength of the W–Cl bond in the organometallic reagent.[25] We were thus gratified to discover during our current investigations that (η^5-C_5H_5)W(NO)$_2BF_4$ is indeed sufficiently electrophilic to cleave a variety of main-group metal to carbon bonds and so produce the desired alkyl or aryl derivatives.

In a manner analogous to reaction 12, the addition of an equimolar amount of Na[BPh_4] to a CH_2Cl_2 solution of (η^5-C_5H_5)W(NO)$_2BF_4$ results in the clean transfer of a phenyl group from B to W, i.e., eq 15, a relatively rare

$$(\eta^5\text{-}C_5H_5)W(NO)_2BF_4 + Na[BPh_4] \xrightarrow{CH_2Cl_2} (\eta^5\text{-}C_5H_5)W(NO)_2Ph + NaBF_4 + BPh_3 \quad (15)$$

mode of reactivity for an organoboron complex.[26] The 48% isolated yield of (η^5-C_5H_5)W(NO)$_2$Ph from this conversion is comparable to that obtained from (η^5-C_5H_5)W(NO)$_2$Cl and Ph_3Al.[10] Reaction 15 probably involves initial anion exchange followed by electrophilic aromatic substitution of BPh_3 by (η^5-C_5H_5)W(NO)$_2$ as depicted in Scheme I. Certainly, the success of this transformation reflects the mediating effect of BPh_3 since, as noted above, (η^5-C_5H_5)W(NO)$_2$Ph cannot be prepared by using highly nucleophilic carbanion sources such as PhLi. Furthermore, the fact that reaction 15 does occur also demonstrates that [BPh_4]$^-$ may not always function as an innocent counterion during the attempted isolation of electrophilic organometallic cations.

Scheme I



where W = (η^5-C_5H_5)W(NO)$_2$

The phenyl derivative of (η^5-C_5H_5)W(NO)$_2$ can also be prepared in moderate yield by employing Ph_4Sn, i.e., eq 16. This transformation is very similar to reaction 15 and

$$(\eta^5\text{-}C_5H_5)W(NO)_2BF_4 + Ph_4Sn \xrightarrow[20\ °C,\ 1\ h]{CH_2Cl_2} (\eta^5\text{-}C_5H_5)W(NO)_2Ph + Ph_3SnBF_4 \quad (16)$$

indicates that this method of forming (η^5-C_5H_5)W(NO)$_2$R complexes is quite general, being limited only by the ready availability of the main-group metal reagent. Consistent with this view is the fact that the analogous use of $(PhCH_2)_4Sn$[27] affords the new benzyl derivative (η^5-C_5H_5)W(NO)$_2CH_2$Ph, i.e., eq 17, although the isolated yield of this stable olive-green solid (18%) is lower than that of the phenyl complex obtained from reaction 16.

$$(\eta^5\text{-}C_5H_5)W(NO)_2BF_4 + (PhCH_2)_4Sn \xrightarrow{CH_2Cl_2} (\eta^5\text{-}C_5H_5)W(NO)_2CH_2Ph + (PhCH_2)_3SnBF_4 \quad (17)$$

As discussed earlier, Et_3Al does not react with (η^5-C_5H_5)W(NO)$_2$Cl. However, it reacts readily with (η^5-C_5H_5)W(NO)$_2BF_4$ at −78 °C, i.e., eq 18, the new tungsten–ethyl complex being isolable in 16% yield from the

$$(\eta^5\text{-}C_5H_5)W(NO)_2BF_4 + Et_3Al \xrightarrow[-78\ °C]{CH_2Cl_2/\text{toluene}} (\eta^5\text{-}C_5H_5)W(NO)_2Et + \{Et_2AlBF_4\} \quad (18)$$

final reaction mixture. [The exact fate of the aluminum has not been ascertained.] This conversion is remarkable because both reactants are Lewis acids. The new (η^5-C_5H_5)W(NO)$_2$R (R = Et or CH_2Ph) complexes exhibit physical properties that are similar to those of their methyl analogue. These green solids are very soluble in organic solvents (including hexanes), and they may be exposed to air for short periods of time without undergoing noticeable decomposition. Without doubt, the failure to prepare these compounds by other preparative routes cannot be attributed to their inherent instability but rather must be as-

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[24] Similar behavior has been observed to occur during the reactions of the isoelectronic (η^5-C_5H_5)Re(CO)(NO)Cl with PhLi or PhMgBr: Sweet, J. R.; Graham, W. A. G. *J. Organomet. Chem.* **1983**, *241*, 45.

[25] (a) Greenhough, T. J.; Kolthammer, B. W. S.; Legzdins, P.; Trotter, J. *Acta Crystallogr., Sect. B* **1980**, *B36*, 795. (b) Morris-Sherwood, B. J.; Kolthammer, B. W. S.; Hall, M. B. *Inorg. Chem.* **1981**, *20*, 2771.

[26] Negishi, E. "Organometallics in Organic Synthesis"; Wiley: New York, 1980; Vol. 1, pp 286–393.

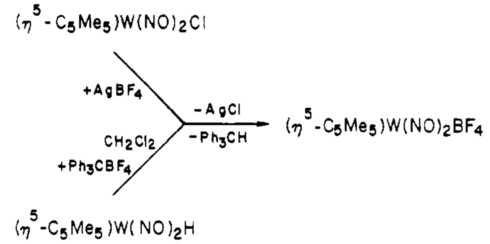
[27] We find that $(PhCH_2)_4Sn$ is best synthesized from $(PhCH_2)_3SnCl$ and $PhCH_2MgCl$ in THF rather than from $SnCl_4$ and $PhCH_2MgCl$ directly since the latter reaction is often accompanied by the formation of substantial amounts of bibenzyl.

cribed to the unsuitability of the previous synthetic methodology. The IR spectra of all the (η^5-C_5H_5)W(NO)$_2$X complexes in CH_2Cl_2 display two strong absorptions assignable to terminal nitrosyl ligands. The frequencies of these absorptions decrease in the order X = Cl > Ph ≈ H > CH_2Ph > Et which reflects the diminishing ability of these ligands to withdraw electron density from the central metal. The chemistry of the various tungsten–alkyl complexes is currently being investigated in detail.

The Related Chemistry of (η^5-C_5Me_5)W(NO)$_2$BF$_4$. We have also extended this chemistry to encompass some of the pentamethylcyclopentadienyl analogues of the complexes discussed in the preceding sections. The new precursor complexes required for this portion of our study can be prepared by straightforward extensions of standard procedures,[4,9] i.e., eq 19 and 20, and their physical properties resemble those of their C_5H_5 analogues. Interestingly, CH_2Cl_2 solutions of (η^5-C_5Me_5)W(NO)$_2$BF$_4$ can be generated from either of these compounds, i.e., eq 21 and 22. Reaction 21 is, of course, the direct analogue of reaction 1, but reaction 22 has no precedent in the C_5H_5 system. [Indeed, treatment of (η^5-C_5H_5)W(NO)$_2$H with Ph_3CBF_4 in CH_2Cl_2 results in the precipitation of [(η^5-C_5H_5)W$_2$(NO)$_4$H]BF$_4$ which is immune to further reaction with Ph_3CBF_4 in this solvent.[3]] The IR spectrum of (η^5-C_5H_5)W(NO)$_2$BF$_4$ in CH_2Cl_2 displays nitrosyl absorptions at 1730 (s) and 1645 (vs) cm^{-1} which are some 20–30 cm^{-1} lower in energy than those exhibited by its cyclopentadienyl analogue. This feature simply reflects the fact that the C_5Me_5 ligand is a better electron donor than the C_5H_5 ligand. Consequently, it can be reasonably anticipated that (η^5-C_5Me_5)W(NO)$_2$BF$_4$ may well be a somewhat weaker electrophile than (η^5-C_5H_5)W(NO)$_2$BF$_4$. Nevertheless, it readily forms an adduct with PPh_3 (cf. eq 4), i.e., eq 23, the product being obtainable in 63% yield. On the other hand, the 5% yield of the new ethyl complex (η^5-C_5Me_5)W(NO)$_2$Et from the conversion shown in eq 24 is less appealing than that of its C_5H_5 analogue from reaction 18.

$$(\eta^5\text{-}C_5Me_5)W(CO)_2(NO) + ClNO \xrightarrow[-78\ ^\circ C]{CH_2Cl_2} (\eta^5\text{-}C_5Me_5)W(NO)_2Cl + 2CO \quad (19)$$

$$(\eta^5\text{-}C_5Me_5)W(NO)_2Cl \xrightarrow[\text{toluene, } -78\ ^\circ C]{Na[AlH_2(OCH_2CH_2OCH_3)_2]} (\eta^5\text{-}C_5Me_5)W(NO)_2H \quad (20)$$



(21)

(22)

$$(\eta^5\text{-}C_5Me_5)W(NO)_2BF_4 + PPh_3 \xrightarrow{CH_2Cl_2} [(\eta^5\text{-}C_5Me_5)W(NO)_2(PPh_3)]BF_4 \quad (23)$$

$$(\eta^5\text{-}C_5Me_5)W(NO)_2BF_4 + Et_3Al \xrightarrow[-78\ ^\circ C]{CH_2Cl_2/\text{toluene}} (\eta^5\text{-}C_5Me_5)W(NO)_2Et + \{Et_2AlBF_4\} \quad (24)$$

Epilogue

This work has shown that the thermally unstable (η^5-C_5H_5)W(NO)$_2$BF$_4$ is a versatile organometallic electrophile that can be employed for the synthesis of a variety of (η^5-C_5H_5)W(NO)$_2$-containing compounds under appropriate experimental conditions. Furthermore, the characteristic chemistry of this complex has established that its component (η^5-C_5H_5)W(NO)$_2^+$ entity is a borderline Lewis acid[28] that interacts strongly only with bases capable of good σ-electron donation. Viewed in this light, the tendency of the [(η^5-C_5H_5)$_2$W(NO)$_4$H]$^+$ cation to undergo cleavage into the monomeric species (η^5-C_5H_5)W(NO)$_2$H and [(η^5-C_5H_5)W(NO)$_2$B]$^+$ when treated with strong Lewis bases, B, is understandable.[3]

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this research in the form of a grant (A5885) to P.L. and to The University of British Columbia for the award of a University Graduate Fellowship to D.T.M.

Registry No. (η^5-C_5H_5)W(NO)$_2$BF$_4$, 87189-85-3; [(η^5-C_5H_5)W(NO)$_2$(PPh$_3$)]BF$_4$, 87189-86-4; [(η^5-C_5H_5)W(NO)$_2${P(OPh)$_3$}]BF$_4$, 87189-87-5; [(η^5-C_5H_5)W(NO)$_2$(η^2-C_8H_{14})]BF$_4$, 87189-89-7; (η^5-C_5H_5)W(NO)$_2$Br, 53419-15-1; (η^5-C_5H_5)W(NO)$_2$H, 69532-01-0; (η^5-C_5H_5)W(NO)$_2$Ph, 57034-44-3; (η^5-C_5H_5)W(NO)$_2$Et, 87189-91-1; (η^5-C_5H_5)W(NO)$_2$CH$_2$Ph, 87189-92-2; (η^5-C_5H_5)W(NO)$_2$OSO$_2$C$_6$H$_4$CH$_3$, 69532-03-2; (η^5-C_5H_5)W(NO)$_2$Cl, 87189-93-3; (η^5-C_5Me_5)W(NO)$_2$H, 87189-94-4; [(η^5-C_5Me_5)W(NO)$_2$(PPh$_3$)]BF$_4$, 87189-96-6; (η^5-C_5Me_5)W(NO)$_2$Et, 87189-97-7; (η^5-C_5Me_5)W(NO)$_2$BF$_4$, 87189-98-8; (η^5-C_5H_5)W(NO)$_2$Cl, 53419-14-0; (η^5-C_5Me_5)W(CO)$_2$(NO), 75212-62-3; [PPN]BF$_4$, 87189-90-0; (PhCH$_2$)$_4$Sn, 10113-29-8; AgBF$_4$, 14104-20-2; Ph$_3$CBr, 596-43-0; [PPN]Br, 20545-30-6; [PPN]BH$_4$, 65013-26-5; Na[BPh$_4$], 143-66-8; Et$_3$Al, 97-93-8; (PhCH$_2$)$_3$SnCl, 3151-41-5; ClNO, 2696-92-6; Na[AlH$_2$(OCH$_2$CH$_2$OCH$_3$)$_2$], 22722-98-1; Ph$_3$CBF$_4$, 341-02-6; 1,1,3-triphenyl-3-methylindan, 19303-32-3; 2,3-dimethyl-2-butene, 563-79-1; 1,1-diphenylethene, 530-48-3; 2,3-dimethyl-1-butene, 563-78-0; benzyl chloride, 100-44-7; silver *p*-toluenesulfonate, 16836-95-6.

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[28] Pearson, R. G. *J. Chem. Educ.* **1968**, *45*, 581, 643.