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New Organometallic Nitrosyl Cations Containing the Group 6 Elements[1,2]

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Treatment of the dihalo nitrosyl complexes of molybdenum and tungsten, $Cp'M(NO)X_2$ (Cp' = Cp (η^5-C_5H_5), Cp* (η^5-C_5Me_5); M = Mo, W; X = Cl, Br, I), in CH_3CN with NO^+ or Ag^+ salts affords a series of new diamagnetic cationic nitrosyl complexes, $[Cp^*Mo(NO)(NCCH_3)_3]^{2+}$ and $[Cp'M(NO)X(NCCH_3)_2]^+$. Eight such complexes have been isolated analytically pure as either their PF_6^- or BF_4^- salts by crystallization from CH_3CN/Et_2O. The physical and spectroscopic properties of these organometallic cations are consistent with their possessing four-legged piano stool molecular structures. This conclusion has been confirmed by single-crystal X-ray crystallographic analyses of $[Cp^*Mo(NO)(NCCH_3)_3][PF_6]_2$ and $[CpMo(NO)Cl(NCCH_3)_2]BF_4$ which also establish that the acetonitrile ligands are coordinated linearly through their N atoms to the metal centers. Crystal data for $[Cp^*Mo(NO)(NCCH_3)_3][PF_6]_2$: monoclinic, a = 32.468 (4) Å, b = 7.7966 (8) Å, c = 10.2999 (17) Å, β = 94.201 (9)°, Z = 4, space group $P2_1/a$, number of unique reflections 5154, number of variables 325, R_F = 0.048, R_{wF} = 0.066. Crystal data for $[CpMo(NO)Cl(NCCH_3)_2]BF_4$: monoclinic, a = 8.4885 (8) Å, b = 16.5569 (19) Å, c = 10.3467 (15) Å, β = 91.753 (9)°, Z = 4, space group $P2_1/c$, number of unique reflections 4101, number of variables 181, R_F = 0.039, R_{wF} = 0.059. ^1H NMR spectroscopy has been employed to demonstrate that the CH_3CN ligands in the $[Cp^*Mo(NO)(NCCH_3)_3]^{2+}$ complex are labile and undergo facile exchange with free CD_3CN solvent molecules. Treatment of $[CpCr(NO)I]_2$ with $AgPF_6$ in CH_3CN affords the novel paramagnetic complex $[CpCr(NO)(NCCH_3)_2]PF_6$. The organometallic cation in this salt is monomeric in the solid state and possesses a three-legged piano stool molecular structure whose intramolecular dimensions have been determined crystallographically. Crystal data for $[CpCr(NO)(NCCH_3)_2]PF_6$: orthorhombic, a = 12.982 (4) Å, b = 6.2962 (6) Å, c = 18.459 (2) Å, Z = 4, space group $Pna2_1$, number of unique reflections 1377, number of variables 189, R_F = 0.034, R_{wF} = 0.044. The room-temperature ESR spectrum of $[CpCr(NO)(NCCH_3)_2]PF_6$ in DMF consists of a broad three-line pattern indicative of the unpaired electron in the 17-electron cation being primarily delocalized onto the nitrosyl ligand ($a(^{14}N)$ = 5.21 G).

Introduction

We have previously established the reduction behavior of the series of organometallic complexes $Cp'Mo(NO)X_2$ (Cp' = Cp (η^5-C_5H_5), Cp* (η^5-C_5Me_5); X = Cl, Br, I) both by cyclic voltammetry and by chemical means.[3] All the $Cp'Mo(NO)X_2$ compounds[4] in CH_2Cl_2 undergo reversible 1-electron reductions, the Cp* derivatives being more difficult to reduce by ca. 0.2 V. On a preparative scale, these reductions are best effected by utilizing Cp_2Co in THF as the reducing agent, i.e.

$$Cp_2Co + Cp'Mo(NO)X_2 \rightarrow [Cp_2Co]^+[Cp'Mo(NO)X_2]^- \qquad (1)$$

The salts resulting from reactions 1 are isolable in high yields as analytically pure, green to brown solids. The ESR spectra of solutions of the $[Cp_2Co]^+[Cp'Mo(NO)X_2]^-$ salts reveal that the unpaired electron density in the 17-valence-electron $[Cp'Mo(NO)X_2]^-$ radical anions is not primarily localized in their Mo–NO linkages, as might have been expected.[3] Rather, the ESR signals due to the unpaired electrons on the anions exhibit coupling either only to the molybdenum center (X = Cl, I) or to both molybdenum and the halide (X = Br). The diiodo radical anions are relatively unstable thermally in DMF and convert to $[Cp'Mo(NO)I]_2$ via I^- loss. The congeneric tungsten complexes $Cp'W(NO)I_2$ behave similarly upon the addition of an electron, converting to $[Cp'W(NO)I]_2$ via EC mechanisms.[3]

During this earlier work we aslo established that these dihalo nitrosyl complexes exhibit irreversible oxidation behavior, a feature generally indicative of the species formed by initial electron removal undergoing further chemical transformation. It thus became of interest to us to establish the exact nature of these transformations by attempting to effect the oxidations with appropriate chemical agents. In this paper we describe the reactions of the $Cp'Mo(NO)X_2$ complexes in CH_3CN with two potential oxidants, namely NO^+ and Ag^+, which lead to new mono- and dicationic nitrosyl complexes. This study has also been extended to encompass the diiodo complexes of tungsten, $Cp'W(NO)I_2$, and the related monoiodo chromium complex, $[CpCr(NO)I]_2$.

Experimental Section

All reactions and subsequent manipulations involving organometallic reagents were performed under anaerobic and anhydrous conditions using an atmosphere of dinitrogen. Conventional Schlenk techniques and a Vacuum Atmospheres Corp. Dri-Lab Model HE-43-2 drybox were employed for the manipulation of air- and moisture-sensitive compounds.[7,8] The halo nitrosyl reagents, $CpMo(NO)Br_2$,[9] $Cp^*W(NO)I_2$,[5] and [CpCr-

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[4] The dihalo nitrosyl complexes $Cp'M(NO)X_2$ (Cp' = Cp, Cp*; M = Mo, W; X = Cl, Br, I) possess either monomeric[5] or halide-bridged dimeric[6] molecular structures in the solid state. However, the physical and chemical properties of these compounds in solutions are most consistent with their existing as solvated monomers.[3] Consequently, in this paper the dichloro complexes are represented exclusively by their monomeric formulae.

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Table I. Analytical Data for Complexes 1–9

complex	no.	yield (%)	anal. found (calcd) C	H	N
$[Cp*Mo(NO)(NCCH_3)_3][PF_6]_2$	1	40	28.75 (29.26)	3.53 (3.66)	8.30 (8.54)
$[Cp*Mo(NO)I(NCCH_3)_2]PF_6$	2	34	26.89 (27.32)	3.34 (3.41)	6.42 (6.83)
$[CpMo(NO)Br(NCCH_3)_2]BF_4$	3	61	24.86 (24.54)	2.60 (2.27)	9.25 (9.54)
$[Cp*Mo(NO)Br(NCCH_3)_2]PF_6$	4	68	29.75 (29.58)	3.79 (3.70)	7.36 (7.39)
$[CpMo(NO)Cl(NCCH_3)_2]BF_4$	5	38	27.22 (27.31)	2.91 (2.78)	10.62 (10.62)
$[Cp*Mo(NO)Cl(NCCH_3)_2]PF_6$	6	20	32.25 (32.09)	4.06 (4.01)	8.20 (8.02)
$[CpW(NO)I(NCCH_3)_2]PF_6$	7	15	17.07 (17.06)	2.11 (1.74)	6.82 (6.63)
$[Cp*W(NO)I(NCCH_3)_2]BF_4$	8	72	26.41 (26.05)	3.32 (3.26)	6.81 (6.51)
$[CpCr(NO)(NCCH_3)_2]PF_6$	9	48	28.88 (28.88)	2.94 (2.93)	11.23 (11.13)

Table II. Infrared Data for Complexes 1–9

complex	no.	ν_{NO} (cm^{-1}) Nujol mull	in CH_3CN	ν_{CN} (cm^{-1}) Nujol mull
$[Cp*Mo(NO)(NCCH_3)_3][PF_6]_2$	1	1718	1680	2320, 2292 (w)
$[Cp*Mo(NO)I(NCCH_3)_2]PF_6$	2	1686	1684	2326, 2295 (w)
$[CpMo(NO)Br(NCCH_3)_2]BF_4$	3	1701	1709	2326, 2297 (w)
$[Cp*Mo(NO)Br(NCCH_3)_2]PF_6$	4	1678	1684	2322, 2295 (w)
$[CpMo(NO)Cl(NCCH_3)_2]BF_4$	5	1705	1707	2328, 2299 (w)
$[Cp*Mo(NO)Cl(NCCH_3)_2]PF_6$	6	1668	1680	2326, 2297 (w)
$[CpW(NO)I(NCCH_3)_2]PF_6$	7	1686	1676	2328, 2299 (w)
$[Cp*W(NO)I(NCCH_3)_2]BF_4$	8	1653	1661	2324, 2293 (w)
$[CpCr(NO)(NCCH_3)_2]PF_6$	9	1709	1710	2326, 2297 (w)

Table III. ^{1}H and ^{13}C{^{1}H} NMR Data (δ) for Complexes 1–8[a]

complex	no.	^{1}H NMR	^{13}C{^{1}H} NMR
$[Cp*Mo(NO)(NCCH_3)_3][PF_6]_2$	1	2.74 (s, 9 H, CH_3CN) 2.18 (s, 15 H, $C_5(CH_3)_5$)	140.30 (CH_3CN) 125.03 ($C_5(CH_3)_5$) 10.61 ($C_5(CH_3)_5$) 4.84 (CH_3CN)
$[Cp*Mo(NO)I(NCCH_3)_2]PF_6$	2	2.65 (s, 6 H, CH_3CN) 2.09 (s, 15 H, $C_5(CH_3)_5$)	140.89 (CH_3CN) 122.63 ($C_5(CH_3)_5$) 11.20 ($C_5(CH_3)_5$) 4.89 (CH_3CN)
$[CpMo(NO)Br(NCCH_3)_2]BF_4$	3	6.52 (s, 5 H, C_5H_5) 2.56 (s, 6 H, CH_3CN)	139.10 (CH_3CN) 112.20 (C_5H_5) 4.63 (CH_3CN)
$[Cp*Mo(NO)Br(NCCH_3)_2]PF_6$	4	2.67 (s, 6 H, CH_3CN) 2.08 (s, 15 H, $C_5(CH_3)_5$)	*b*
$[CpMo(NO)Cl(NCCH_3)_2]BF_4$	5	6.51 (s, 5 H, C_5H_5) 2.54 (s, 6 H, CH_3CN)	137.63 (CH_3CN) 112.52 (C_5H_5) 4.46 (CH_3CN)
$[Cp*Mo(NO)Cl(NCCH_3)_2]PF_6$	6	2.65 (s, 6 H, CH_3CN) 2.07 (s, 15 H, $C_5(CH_3)_5$)	137.11 (CH_3CN) 123.33 ($C_5(CH_3)_5$)· 10.68 ($C_5(CH_3)_5$) 4.48 (CH_3CN)
$[CpW(NO)I(NCCH_3)_2]PF_6$	7	6.45 (s, 5 H, C_5H_5) 1.96 (s, 6 H, CH_3CN)	*b*
$[Cp*W(NO)I(NCCH_3)_2]BF_4$	8	2.74 (s, 6 H, CH_3CN) 2.21 (s, 15 H, $C_5(CH_3)_5$)	139.93 (CH_3CN) 118.37 ($C_5(CH_3)_5$) 10.76 ($C_5(CH_3)_5$) 5.16 (CH_3CN)

[a] All spectra presented are for the complexes in CD_3NO_2 except for 7 which is in CD_3CN. [b] ^{13}C{^{1}H} NMR spectrum not obtained.

$(NO)I]_2$,[10] were prepared by published procedures. The permethylated complexes, $Cp*Mo(NO)X_2$ (X = Br, I), were prepared by treating $Cp*Mo(CO)_2(NO)$ with X_2 in a manner similar to that employed for the preparation of their Cp analogues. Both $Cp'Mo(NO)Cl_2$ (Cp′ = Cp, Cp*) complexes were synthesized by treating the corresponding $Cp'Mo(CO)_2(NO)$ species with an equimolar amount of PCl_5 in Et_2O.[6b] All other reagents used were of reagent grade or comparable purity and were purchased from commercial suppliers. Reagent purity was ascertained by elemental analysis and ^{1}H NMR spectroscopy. Solvents were dried according to conventional procedures,[11] distilled, and deaerated with dinitrogen just prior to use. All reactions were effected at ambient temperatures.

Infrared spectra were recorded on a Nicolet 5DX FT-IR instrument which was internally calibrated with a He/Ne laser. All ^{1}H and ^{13}C NMR spectra were obtained on a Varian Associates XL-300 or a Bruker WP-80 spectrometer with reference to the residual ^{1}H or ^{13}C signal of the solvent employed. All ^{1}H and ^{13}C chemical shifts are reported in parts per million (ppm) downfield from Me_4Si. Ms. M. Austria, Ms. L. Darge, and Dr. S. O. Chan assisted in the collection of the NMR spectra. The ESR spectrum was recorded by Professor F. G. Herring of this department using his spectrometer and interfaced computer system.[12] Low-resolution mass spectra were recorded at 70 eV on a Kratos MS50 spectrometer using the direct-insertion method by Dr. G. K. Eigendorf and the staff of the U.B.C. Mass Spectrometry Laboratory. Elemental analyses were performed by Mr. P. Borda of this department.

Preparation of $[Cp*Mo(NO)(NCCH_3)_3][PF_6]_2$ (1). A stirred solution of $Cp*Mo(NO)I_2$ (1.18 g, 2.29 mmol) in CH_3CN (60 mL) was treated dropwise with a solution of $NOPF_6$ (0.401 g, 2.29 mmol) in CH_3CN (15 mL). The reaction mixture was stirred for 40 min during which time the color of the solution changed from dark reddish brown to light brown. The progress of the reaction was monitored by IR spectroscopy which revealed that the ν_{NO} of $Cp*Mo(NO)I_2$ at 1660 cm^{-1} gradually decreased in intensity with the concomitant growth of a new nitrosyl band at 1680 cm^{-1}. The volume of the solvent in the final reaction mixture was then reduced to 10 mL in vacuo. Addition of Et_2O (120 mL) precipitated $[Cp*Mo(NO)(NCCH_3)_3][PF_6]_2$, complex 1, as an air-stable, yellow, microcrystalline solid (0.617 g, 0.915 mmol, 40% yield). The analytical, IR, and NMR data for this compound and the other new compounds synthesized in this work are collected in Tables I–III.

The dicationic complex 1 could also be obtained in similar yield by treating $Cp*Mo(NO)I_2$ with 2 equiv of $AgPF_6$ in CH_3CN. The final reaction mixture was filtered through a column of Celite (2 × 2 cm) supported on a medium-porosity frit. Workup of the resulting yellow filtrate was as described above.

Large oval-shaped crystals of $[Cp*Mo(NO)(NCCH_3)_3][PF_6]_2$ (1) suitable for X-ray crystallographic analysis were grown by maintaining a saturated CH_3CN/Et_2O solution of the complex at 0 °C for 7 days.

Preparation of $[Cp*Mo(NO)I(NCCH_3)_2]PF_6$ (2). Solid $AgPF_6$ (0.256 g, 1.01 mmol) was added to a stirred CH_3CN solution (20 mL) of $Cp*Mo(NO)I_2$ (0.520 g, 1.01 mmol). The color of the reaction mixture changed from dark reddish brown to dark yellow, and a yellow-white precipitate formed. After 30 min, an IR spectrum of the supernatant solution revealed the complete consumption of the starting organometallic complex (ν_{NO} 1660 cm^{-1}) and the formation of the new nitrosyl-containing compound (ν_{NO} 1684 cm^{-1}). The final reaction mixture was filtered through a column of Celite (2 × 3 cm) supported on a medium-porosity frit. The dark yellow filtrate thus obtained was concentrated to 5 mL under reduced pressure, layered with Et_2O (40 mL), and maintained at 0 °C for 12 h. The microcrystalline solid that

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deposited was collected by filtration and dried in vacuo (5×10^{-3} mm) for 5–6 h. This procedure afforded 0.21 g (0.34 mmol, 34% yield) of [Cp*Mo(NO)I($NCCH_3$)$_2$]PF_6, complex **2**, as an analytically pure, dark yellow microcrystalline solid.

Preparation of [CpMo(NO)Br($NCCH_3$)$_2$]BF_4 (3). To a stirred CH_3CN solution (40 mL) of CpMo(NO)Br_2 (1.22 g, 3.47 mmol) was added solid $AgBF_4$ (0.67 g, 3.4 mmol). The color of the solution changed instantaneously from light brown to dark orange, and a creamy, light yellow precipitate formed. After 30 min, an IR spectrum of the supernatant solution revealed the complete consumption of CpMo(NO)Br_2 (ν_{NO} 1686 cm^{-1}) and the formation of a new product (ν_{NO} 1709 cm^{-1}). Subsequent workup of the reaction mixture was as described above for the isolation of complex **2**. This procedure afforded 0.92 g (2.1 mmol, 61% yield) of [CpMo(NO)Br($NCCH_3$)$_2$]BF_4, complex **3**, as a light brown, microcrystalline solid.

[CpMo(NO)Br($NCCH_3$)$_2$]PF_6 could also be synthesized by treatment of CpMo(NO)Br_2 with an equimolar amount of $NOPF_6$ in CH_3CN, but the transformation did not proceed cleanly and the final cationic product was obtained in very low isolated yield (ca. 5%).

Preparation of [Cp*Mo(NO)Br($NCCH_3$)$_2$]PF_6 (4). A stirred CH_3CN solution (40 mL) of Cp*Mo(NO)Br_2 (0.26 g, 0.62 mmol) was treated dropwise with a solution of $NOPF_6$ (0.107 g, 0.611 mmol) in CH_3CN (10 mL), and the progress of the reaction was monitored by IR spectroscopy. The intensity of the nitrosyl band due to Cp*Mo(NO)Br_2 (ν_{NO} 1659 cm^{-1}) slowly decreased with an increase in the intensity of a new nitrosyl band at 1684 cm^{-1}. After 2 h, the reaction mixture was treated in a manner similar to that described above for the isolation of complex **1**. By this procedure, complex **4**, [Cp*Mo(NO)Br($NCCH_3$)$_2$]PF_6, was isolated as a dark yellow microcrystalline solid in 68% yield (0.24 g, 0.42 mmol).

Preparation of [CpMo(NO)Cl($NCCH_3$)$_2$]BF_4 (5). Solid $AgBF_4$ (0.280 g, 1.44 mmol) was added to a stirred CH_3CN solution (30 mL) of CpMo(NO)Cl_2 (0.38 g, 1.4 mmol). The color of the reaction mixture changed from dark orange-brown to dark yellow, and a white solid precipitated. After 30 min, an IR spectrum of the supernatant solution revealed that the organometallic reactant (ν_{NO} 1680 cm^{-1}) had been completely consumed and that a new complex (ν_{NO} 1707 cm^{-1}) had been formed. Subsequent workup of the reaction mixture was as for **2**. In this manner 0.22 g (0.56 mmol, 38% yield) of analytically pure, yellow-orange crystals of [CpMo(NO)Cl($NCCH_3$)$_2$]BF_4, complex **5**, was obtained.

[CpMo(NO)Cl($NCCH_3$)$_2$]PF_6 could also be obtained by the treatment of CpMo(NO)Cl_2 with $NOPF_6$ in CH_3CN, but this route afforded the organometallic salt in very low isolated yield (<5%).

Large crystals of [CpMo(NO)Cl($NCCH_3$)$_2$]BF_4 suitable for X-ray crystallographic analysis were obtained by maintaining a saturated CH_3CN/Et_2O solution of the salt at −25 °C for 7 days.

Preparation of [Cp*Mo(NO)Cl($NCCH_3$)$_2$]PF_6 (6). A CH_3CN solution (10 mL) of $NOPF_6$ (0.208 g, 1.19 mmol) was added dropwise to a stirred solution of Cp*Mo(NO)Cl_2 (0.380 g, 1.24 mmol) in CH_3CN (30 mL). The color of the reaction mixture gradually changed from light brown to a lighter brown. The progress of the reaction was monitored by IR spectroscopy which revealed that the intensity of the ν_{NO} of Cp*Mo(NO)Cl_2 (1652 cm^{-1}) gradually decreased with the concomitant growth of a new nitrosyl band at 1680 cm^{-1}. After 2.5 h, the final reaction mixture was treated as described above for the isolation of complex **1**. This methodology afforded analytically pure, light brown-orange crystals of [Cp*Mo(NO)Cl($NCCH_3$)$_2$]PF_6, complex **6** (0.11 g, 0.22 mmol, 20% yield).

Preparation of [CpW(NO)I($NCCH_3$)$_2$]PF_6 (7). A stirred CH_3CN solution (60 mL) of CpW(NO)I_2 (0.67 g, 1.26 mmol) was treated dropwise with a solution of $NOPF_6$ (0.21 g, 1.20 mmol) in CH_3CN (15 mL). The reaction mixture was stirred for 6 h, during which time the color of the solution changed from light brown-orange to light brown-green. Subsequent workup of the reaction mixture was as for complex **1**. This procedure provided 0.12 g (0.20 mmol, 15% yield) of analytically pure, yellowish green crystals of [CpW(NO)I($NCCH_3$)$_2$]PF_6 (**7**).

Preparation of [Cp*W(NO)I($NCCH_3$)$_2$]BF_4 (8). To a stirred CH_3CN solution (30 mL) of Cp*W(NO)I_2 (0.750 g, 1.24 mmol) was added $AgBF_4$ (0.242 g, 1.24 mmol). The color of the solution changed immediately from dark orange-red to dark yellow with the concomitant formation of a creamy yellow precipitate. After 30 min, an IR spectrum of the supernatant solution revealed that reaction was complete. The reaction mixture was filtered through a column of Celite (2 × 2 cm) supported on a frit, and the filtrate was concentrated under reduced pressure to 10 mL. Addition of Et_2O (40 mL) resulted in the precipitation of a dark yellow solid which was collected by filtration, washed with Et_2O (2 × 10 mL), and dried in vacuo (5×10^{-3} mm) for 5–6 h. This procedure afforded 0.58 g (0.89 mmol, 72% yield) of dark yellow [Cp*W(NO)I($NCCH_3$)$_2$]BF_4 (**8**).

Preparation of [CpCr(NO)($NCCH_3$)$_2$]PF_6 (9). To a stirred solution of [CpCr(NO)I]$_2$ (0.780 g, 1.42 mmol) in acetonitrile (30 mL) was added $AgPF_6$ (0.720 g, 2.80 mmol). The color of the solution immediately changed from dark olive green to bright green, a change that was accompanied by the formation of a yellow-white precipitate. After the reaction mixture had been stirred for 30 min, an IR spectrum of the supernatant solution indicated the complete consumption of the starting organometallic reactant (ν_{NO} 1680 cm^{-1}) and the formation of a new nitrosyl-containing compound (ν_{NO} 1710 cm^{-1}). The final reaction mixture was filtered through a column of Celite (2 × 2 cm) supported on a medium-porosity glass frit. The bright green filtrate was concentrated to ca. 5 mL in vacuo. Addition of diethyl ether (20 mL) induced the precipitation of a green microcrystalline solid that was collected by filtration and washed with diethyl ether (2 × 20 mL). The bright green solid was dried in vacuo (5×10^{-3} mm) at room temperature for 12 h to obtain analytically pure [CpCr(NO)($NCCH_3$)$_2$]PF_6, complex **9** (0.50 g, 1.40 mmol, 49% yield).

Large crystals of [CpCr(NO)($NCCH_3$)$_2$]PF_6 (**9**) suitable for X-ray crystallographic analysis were obtained by maintaining a saturated CH_3CN/Et_2O solution of the complex at −25 °C for 2 weeks.

A DMF solution of complex **9** used for ESR measurements was prepared as follows. The DMF solvent was first dried over anhydrous BaO for 24 h, filtered through Celite, and then purged with N_2. In a glovebox was dissolved a weighed amount of **9** in enough DMF to make up a 5×10^{-5} M solution. A small portion of the resulting green solution was transferred into a melting point capillary tube via a syringe. The capillary tube was then sealed with high-vacuum grease.

X-ray Crystallographic Analyses of [Cp*Mo(NO)($NCCH_3$)$_3$][PF_6]$_2$ (1), [CpMo(NO)Cl($NCCH_3$)$_2$]BF_4 (5), and [CpCr(NO)($NCCH_3$)$_2$]PF_6 (9). The X-ray structure determinations of the three complexes were performed in a similar manner. A suitable X-ray-quality crystal of each complex was obtained as described in the preceding paragraphs. Each crystal was mounted in a thin-walled glass capillary under N_2 and transferred to an Enraf-Nonius CAD4-F diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda_{K\alpha_1} = 0.70930$, $\lambda_{K\alpha_2} = 0.71359$ Å). Final unit cell parameters for each complex were obtained by least-squares analysis of $2(\sin\theta)/\lambda$ values for 25 well-centered reflections, i.e., $19.1 \leq \theta \leq 22.2°$ for **1**, $22.2 \leq \theta \leq 24.9°$ for **5**, and $7.9 \leq \theta \leq 14.6°$ for **9**. The intensities of three standard reflections were measured every 1 h of X-ray exposure time during the data collection. The intensities of the standard reflections of **1** and **9** showed no appreciable variations in intensity with time, but those of **5** exhibited some decrease (11%), and the latter data were scaled for this deterioration in crystal quality. The data were corrected for Lorentz and polarization effects and for absorption using the Gaussian integration method.[13-15] Pertinent crystallographic and experimental parameters for the three complexes are summarized in Table IV.

Interpretation of the Patterson function yielded the coordinates of the heaviest atoms in each structure, and the full structures of all three compounds were then derived by conventional electron density methods and refined by full-matrix least-squares methods on F, minimizing the function $w(|F_o| - |F_c|)^2$, where $w = [\sigma^2(F)]^{-1}$.

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(13) The computer programs used include locally written programs for data processing and locally modified versions of the following: ORFLS, full-matrix least squares, and ORFFE, function and errors, by W. R. Busing, K. O. Martin, and H. A. Levy; FORDAP, Patterson and Fourier syntheses, by A. Zalkin; ORTEPII, illustrations, by C. K. Johnson.

(14) Coppens, P.; Leiserowitz, L.; Rabinovich, D. *Acta Crystallogr.* **1965**, *18*, 1035.

(15) Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1967**, *22*, 457.

Table IV. Crystallographic and Experimental Data[a] for the Complexes $[Cp^*Mo(NO)(NCCH_3)_3][PF_6]_2$ (1), $[CpMo(NO)Cl(NCCH_3)_2]BF_4$ (5), and $[CpCr(NO)(NCCH_3)_2]PF_6$ (9)

	1	5	9
color	orange	yellow-orange	green
formula	$C_{16}H_{24}F_{12}N_4OP_2Mo$	$C_9H_{11}BClF_4N_3OMo$	$C_9H_{11}F_6N_3OPCr$
formula weight	674.26	395.40	374.17
crystal system	monoclinic	monoclinic	orthorhombic
space group	$P2_1/a$	$P2_1/c$	$Pna2_1$
a (Å)	32.468 (4)	8.4885 (8)	12.982 (4)
b (Å)	7.7966 (8)	16.5569 (19)	6.2962 (6)
c (Å)	10.2999 (17)	10.3467 (15)	18.459 (2)
α (deg)	90	90	90
β (deg)	94.201 (9)	91.753 (9)	90
γ (deg)	90	90	90
V (Å^3)	2600.3 (6)	1453.5 (5)	1508.8 (7)
Z	4	4	4
d_{calcd} (Mg/m^3)	1.73	1.81	1.65
$F(000)$	1344	560	748
μ(Mo Kα) (cm^{-1})	7.1	11.1	9.1
T(K)	293	293	293
crystal dimensions (mm^3)	0.19 × 0.25 × 0.48	0.15 × 0.25 × 0.60	0.06 × 0.33 × 0.38
transmission factors	0.82–0.89	0.76–0.85	0.77–0.95
scan type	ω–2θ	ω–2θ	ω–2θ
scan range (deg)	0.65 + 0.35 tan θ	0.75 + 0.35 tan θ	0.60 + 0.35 tan θ
scan speed (deg/min)	1.3–10	1.5–20	1.2–20
2θ limits (deg)	$0 \le 2\theta \le 55$	$0 \le 2\theta \le 60$	$0 \le 2\theta \le 50$
data collected	$+h,-k,\pm l$	$\pm h,+k,+l$	$-h,+k,+l$
unique reflections	5154	4101	1377
reflections with $I > 3\sigma(I)$	3201	2862	788
no. of variables	325	181	189
R_F[b]	0.048	0.039	0.034
R_{wF}[c,d]	0.066	0.059	0.044
goodness of fit[e]	2.03	2.00	1.39
max Δ/σ (final cycle)	0.04	0.04	3.9[f]
residual density (e/Å^3)	−0.49 to +0.60	−0.60 to +0.79	−0.18 to +0.25

[a] Enraf-Nonius CAD4-F diffractometer, Mo Kα radiation, graphite monochromator. [b] $R_F = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum F_o^2]^{1/2}$. [d] $w = [\sigma^2(F)]^{-1}$. [e] GOF $= [\sum w(|F_o| - |F_c|)^2/(\text{no. of degrees of freedom})]^{1/2}$. [f] Residual oscillatory shifts in the F parameters.

Hydrogen atoms were placed in idealized positions based on difference maps, with thermal parameters $B = 1.2B$ (bonded atom), and were not refined, but were repositioned after each cycle. Final refinements were carried out with non-hydrogen atoms being permitted anisotropic thermal motion. The polarity of the crystal of 9 was not determined. Complex neutral atom scattering factors were taken from ref 16. Final positional and equivalent isotropic thermal parameters ($U_{eq} = {}^1/_3 \times$ trace diagonalized U) for the complexes are given in Table V, and selected bond lengths (Å) and bond angles (deg) are listed in Table VI. Anisotropic thermal parameters, hydrogen parameters, full listings of molecular dimensions, tables of calculated and observed structure factors, and packing diagrams for 1, 5, and 9 are provided as supplementary material. Stereoviews of the solid-state molecular structures of the three complexes, 1, 5, and 9, are displayed in Figures 1–3, respectively.

Results and Discussion

Syntheses and Characterization of the Diamagnetic Complexes 1–8. The complexes 1–8 containing diamagnetic organometallic cations are preparable by the treatment of the appropriate $Cp'M(NO)X_2$ precursor complexes with either NO^+ or Ag^+ salts in CH_3CN. The progress of the various transformations to completion may be conveniently monitored by IR spectroscopy, as outlined in the Experimental Section. All the complexes are obtainable analytically pure by crystallization from CH_3CN/Et_2O solutions. The physical and spectroscopic data for the compounds are collected in Tables I–III. The specific preparations and physical properties of each of these complexes are considered in turn below.

$[Cp^*Mo(NO)(NCCH_3)_3][PF_6]_2$, Complex 1. Treatment of $Cp^*Mo(NO)I_2$ with 1 equiv of $NOPF_6$ in CH_3CN consumes the organometallic reactant completely. From the final reaction mixture, $[Cp^*Mo(NO)(NCCH_3)_3][PF_6]_2$ (1) is isolable in 40% yield.

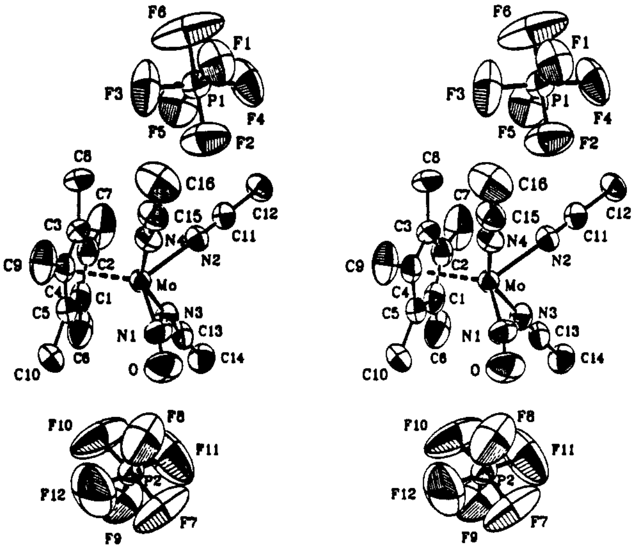

Figure 1. Stereoview of the solid-state molecular structure of $[Cp^*Mo(NO)(NCCH_3)_3][PF_6]_2$ (1), hydrogen atoms having been omitted for clarity.

$$Cp^*Mo(NO)I_2 \text{ in } CH_3CN \xrightarrow{NO^+} [Cp^*Mo(NO)(NCCH_3)_3][PF_6]_2 \quad (2)$$

In order to obtain uncontaminated $[Cp^*Mo(NO)(NCCH_3)_3][PF_6]_2$ in respectable yields, it is important that the CH_3CN solution of the $NOPF_6$ reagent be added slowly in a dropwise manner to the solution of the $Cp^*Mo(NO)I_2$

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(16) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.

Table V. Final Positional (Fractional × 10^4; Mo, P, Cl, and Cr × 10^5) and Equivalent Isotropic Thermal Parameters (U_{eq} × 10^3 Å^2) for the Non-Hydrogen Atoms of the Complexes $[Cp^*Mo(NO)(NCCH_3)_3][PF_6]_2$ (1), $[CpMo(NO)Cl(NCCH_3)_2]BF_4$ (5), and $[CpCr(NO)(NCCH_3)_2]PF_6$ (9) with Estimated Standard Deviations in Parentheses

	x	*y*	*z*	U_{eq}		*x*	*y*	*z*	U_{eq}
				$[Cp^*Mo(NO)(NCCH_3)_3][PF_6]_2$					
Mo	60576 (2)	40921 (6)	73557 (5)	43	C6	5659 (4)	5 (12)	7993 (11)	113
O	5304 (2)	5911 (8)	6343 (7)	97	C7	6630 (4)	716 (14)	8760 (10)	128
N1	5606 (2)	5320 (7)	6810 (6)	59	C8	6975 (2)	2593 (13)	6378 (10)	93
N2	6428 (2)	5407 (7)	8890 (5)	55	C9	6224 (3)	3175 (11)	4190 (7)	93
N3	5740 (2)	3455 (7)	9033 (5)	57	C10	5417 (3)	1719 (16)	5279 (11)	119
N4	6391 (2)	5858 (7)	6256 (5)	56	C11	6630 (2)	5986 (8)	9703 (6)	52
C1	5946 (3)	1075 (9)	7257 (7)	70	C12	6884 (2)	6787 (9)	10756 (6)	64
C2	6370 (2)	1324 (8)	7557 (6)	61	C13	5555 (2)	3254 (8)	9899 (7)	62
C3	6534 (2)	2184 (9)	6511 (7)	59	C14	5319 (3)	2956 (11)	11052 (9)	84
C4	6191 (2)	2475 (8)	5546 (6)	54	C15	6558 (2)	6801 (10)	5645 (7)	64
C5	5833 (2)	1796 (9)	6031 (7)	61	C16	6778 (3)	7993 (13)	4831 (9)	102
P1	23063 (6)	29591 (25)	22332 (18)	64	F6	1833 (2)	3304 (18)	2075 (9)	226
P2	6901 (7)	71677 (26)	21458 (21)	71	F7	1018 (3)	8577 (14)	2182 (12)	213
F1	2233 (2)	1255 (7)	3029 (5)	112	F8	362 (3)	8405 (9)	2559 (12)	212
F2	2786 (2)	2639 (12)	2342 (6)	143	F9	1003 (3)	5878 (10)	1641 (13)	198
F3	2350 (3)	3912 (8)	3557 (6)	148	F10	379 (3)	5756 (10)	2223 (16)	242
F4	2278 (2)	1960 (8)	916 (5)	137	F11	588 (4)	7662 (20)	778 (8)	263
F5	2386 (2)	4618 (8)	1433 (6)	131	F12	809 (4)	6731 (21)	3494 (9)	271
				$[CpMo(NO)Cl(NCCH_3)_2]BF_4$					
Mo	12433 (4)	38814 (2)	29233 (3)	38	C3	1363 (17)	3279 (5)	953 (6)	131
Cl	25240 (15)	40062 (8)	50309 (11)	57	C4	2290 (8)	2834 (5)	1683 (9)	96
O	−75 (4)	5411 (2)	1874 (4)	80	C5	1482 (12)	2469 (3)	2536 (7)	95
N1	502 (4)	4841 (2)	2389 (4)	50	C6	−1741 (5)	3811 (2)	4856 (5)	47
N2	−747 (4)	3807 (2)	4170 (4)	46	C7	−3051 (6)	3810 (3)	5720 (5)	61
N3	3539 (4)	4293 (2)	2427 (4)	48	C8	4752 (5)	4525 (3)	2204 (4)	47
C1	−33 (16)	2685 (8)	2346 (14)	176	C9	6321 (5)	4822 (4)	1966 (6)	66
C2	−113 (13)	3206 (7)	1323 (15)	173					
B	6024 (6)	1746 (4)	4227 (6)	60	F3	6560 (8)	2379 (3)	3638 (5)	183
F1	5967 (5)	1895 (3)	5531 (3)	104	F4	4599 (6)	1589 (4)	3793 (7)	167
F2	6933 (6)	1095 (3)	4037 (5)	149					
				$[CpCr(NO)(NCCH_3)_2]PF_6$					
Cr	32031 (7)	38953 (16)	10000	49	C3	4825 (10)	3028 (22)	1341 (9)	69
O	1633 (5)	7125 (10)	978 (15)	116	C4	4558 (18)	5000 (52)	1598 (13)	143
N1	2246 (4)	5702 (10)	1012 (11)	71	C5	4315 (11)	6459 (18)	929 (30)	197
N2	2644 (12)	1965 (24)	1785 (9)	67	C6	2365 (16)	833 (27)	2217 (12)	56
N3	2643 (9)	1987 (22)	234 (6)	60	C7	1914 (15)	−392 (32)	2751 (11)	99
C1	4469 (15)	5315 (52)	456 (15)	140	C8	2276 (12)	961 (28)	−195 (10)	69
C2	4722 (14)	3566 (39)	570 (9)	132	C9	1905 (14)	−546 (30)	−758 (10)	71
P	5005 (5)	20 (14)	3491 (4)	58	F4	5542 (9)	1696 (19)	4016 (7)	151
F1	5830 (10)	285 (23)	2900 (6)	134	F5	4332 (9)	1754 (21)	3140 (6)	120
F2	4039 (8)	−323 (19)	4001 (7)	109	F6	5514 (12)	−2102 (18)	3768 (6)	136
F3	4522 (12)	−1273 (27)	2911 (6)	157					

Table VI. Selected Bond Lengths (Å) and Bond Angles (deg) for the Complexes $[Cp^*Mo(NO)(NCCH_3)_3][PF_6]_2$ (1), $[CpMo(NO)Cl(NCCH_3)_2]BF_4$ (5), and $[CpCr(NO)(NCCH_3)_2]PF_6$ (9)

	1 (M = Mo)	**5** (M = Mo)	**9** (M = Cr)
M—NC	2.172 (5) (trans to NO) 2.131 (6) (cis to NO)	2.160 (3) 2.141 (3)	2.025 (16) 1.993 (12)
M—NO	1.805 (5)	1.790 (4)	1.685 (6)
M—CP[a]	2.025 (3)	2.032 (5)	1.851 (8)
M—Cl		2.416 (1)	
N≡C	1.13 (1)	1.124 (5)	1.13 (2)
NC—CH_3	1.47 (1)	1.448 (6)	1.44 (3)
N—O	1.16 (1)	1.183 (5)	1.17 (1)
P—F	1.45–1.59 (1)		1.48–1.59 (1)
B—F		1.30–1.37 (1)	
M—N—C	173.8–177.8 (5)	175.6, 177.6 (4)	177 (2)
N≡C—CH_3	178.4 (8)	178.4 (5)	173 (2)
M—N—O	170.2 (6)	169.8 (4)	172 (1)
CP—M—L	103.1–126.8 (2)	101.1–129.4 (2)	119.7–122.2 (5)
L—M—L	111.7 (2) (trans) 151.2 (2) (trans) 78.2–86.9 (2) (cis)	110.3 (1) (trans) 153.5 (1) (trans) 78.6–87.8 (2) (cis)	90.9–98.5 (6)

[a] CP = centroid of cyclopentadienyl ring.

complex. Otherwise, reaction 2 is often accompanied by the formation of other nitrosyl-containing byproducts, a feature which lowers the isolated yield of the desired product substantially. Alternatively, the dicationic complex 1 can also be synthesized in similar yield by treating $Cp^*Mo(NO)I_2$ with 2 equiv of $AgPF_6$ in CH_3CN, i.e.

$$Cp^*Mo(NO)I_2 \text{ in } CH_3CN \xrightarrow[-2AgI]{2Ag^+} [Cp^*Mo(NO)(NCCH_3)_3][PF_6]_2 \quad (3)$$

Pure $[Cp^*Mo(NO)(NCCH_3)_3][PF_6]_2$ is a yellow microcrystalline solid which is thermally stable at room temperature in the solid state under N_2 for several months. As a solid, it can be handled in air for several hours without the occurrence of any noticeable decomposition. The complex is only sparingly soluble in THF, but quite soluble in acetone, acetonitrile, and nitromethane to yield air-sensitive yellow solutions.

The IR spectra of 1, either as a Nujol mull or as a CH_3CN solution, exhibit strong absorptions attributable to the terminal nitrosyl ligand. The nitrosyl stretching frequency of complex 1 (1718 cm^{-1} as a Nujol mull) occurs at a higher frequency than that of its neutral precursor $Cp^*Mo(NO)I_2$ (1645 cm^{-1}), a feature indicative of a substantial decrease in back-bonding to the nitrosyl ligand in the cation. In addition to the nitrosyl band, the Nujol mull IR spectrum of 1 also exhibits two weak bands at 2320 and 2292 cm^{-1} in the ν_{CN} region of the coordinated acetonitrile

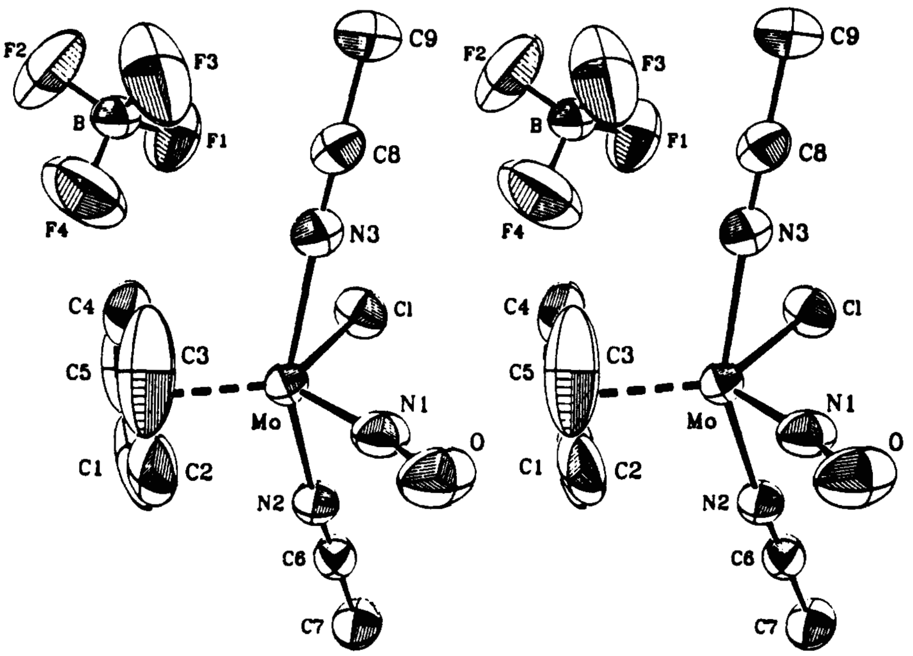

Figure 2. Stereoview of the solid-state molecular structure of $[CpMo(NO)Cl(NCCH_3)_2]BF_4$ (**5**), hydrogen atoms having been omitted for clarity.

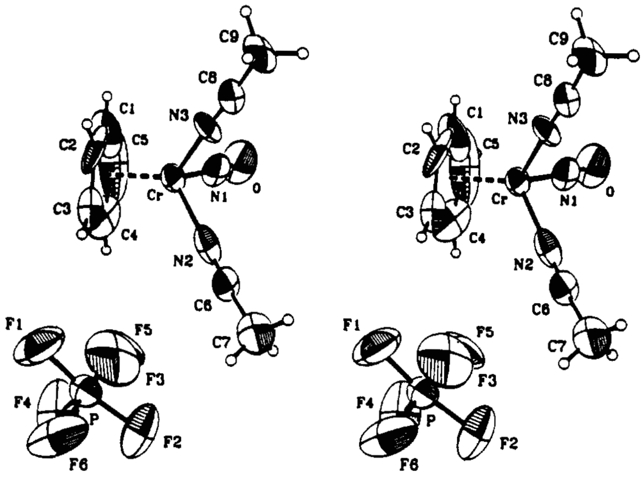

Figure 3. Stereoview of the solid-state molecular structure of $[CpCr(NO)(NCCH_3)_2]PF_6$ (**9**).

ligands.[17] These bands are comparable to those observed for the dicationic complex, $[Cp_2Ti(NCCH_3)_2][PF_6]_2$ (ν_{CN} 2325 and 2288 cm^{-1}).[18]

The ^1H NMR spectrum of **1** in CD_3NO_2 indicates its organometallic cation to be stereochemically nonrigid in solution since it exhibits singlets at δ 2.74 and 2.18 due to the protons of the three equivalent CH_3CN ligands and the Cp* ligand, respectively. The proton resonance of the CH_3CN ligands is shifted 0.74 ppm downfield from that of free CH_3CN (δ 2.00 in CD_3NO_2). The downfield shift which accompanies the coordination of the CH_3CN to the metal center has also been observed in other cationic metal acetonitrile complexes.[18,19] The three CH_3CN ligands in complex **1** also show considerable lability in solution at 25 °C. Thus, the ^1H NMR spectrum of a freshly prepared solution of $[Cp^*Mo(NO)(NCCH_3)_3][PF_6]_2$ in CD_3CN exhibits a weak resonance at δ 1.93 due to the protons of free CH_3CN along with a larger peak at δ 2.58 for the coordinated CH_3CN. After several hours at room temperature, the signal at δ 2.58 disappears completely, whereas that at 1.93 ppm increases in intensity. These observations are indicative of an exchange process between the coordinated CH_3CN and free CD_3CN molecules, i.e.

$$[Cp^*Mo(NO)(NCCH_3)_3][PF_6]_2 + \text{excess } CD_3CN \rightarrow [Cp^*Mo(NO)(NCCD_3)_3][PF_6]_2 \quad (4)$$

This observation is significant since it has been previously demonstrated that the ability of some cationic transition-metal nitrosyl complexes with coordinated acetonitrile ligands to catalyze the oligomerization and polymerization of olefins is due both to the electrophilic nature of the cation as well as to the lability of their acetonitrile ligands in solution (vide infra).

In order to remove any possible ambiguities about the true nature of $[Cp^*Mo(NO)(NCCH_3)_3][PF_6]_2$, the complex has been subjected to a single-crystal X-ray crystallographic analysis. Its solid-state molecular structure is shown in Figure 1, and listings of selected bond lengths and bond angles are presented in Table VI. The crystal structure of $[Cp^*Mo(NO)(NCCH_3)_3][PF_6]_2$ consists of the packing of discrete $[Cp^*Mo(NO)(NCCH_3)_3]^{2+}$ cations and PF_6^- anions with no unusual cation–anion contacts. As is evident from Figure 1, the coordination geometry about the central molybdenum atom is that of a four-legged piano stool. A direct comparison of the metrical parameters of complex **1** and other dicationic complexes containing the Cp*Mo(NO) fragment cannot be made since **1** is the first species of its kind to have been structurally characterized. Nevertheless, the structural features of complex **1** may be compared to those of the closely related cationic complex, $[\{HB(Me_2pz)_3\}Mo(NO)(NCCH_3)_2]PF_6$.[20] The Mo–N–O linkage in **1** is essentially linear, although slightly more bent than in $[\{HB(Me_2pz)_3\}Mo(NO)(NCCH_3)_2]PF_6$ (170.2 (6)° vs 173.4 (8)°). The Mo–NO bond (1.805 (5) Å) is longer and the N–O bond (1.158 (7) Å) is shorter than the corresponding bond lengths in $[\{HB(Me_2pz)_3\}Mo(NO)(NCCH_3)_2]PF_6$. The three acetonitrile ligands are N-bonded to the Mo center in **1** in a linear $MoN{\equiv}CCH_3$

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[17] Storhoff, B. N.; Lewis, H. C., Jr. *Coord. Chem. Rev.* **1977**, *23*, 1.

[18] Bruce, M. R. M.; Tyler, D. R. *Organometallics* **1985**, *4*, 528.

[19] Sen, A.; Thomas, R. R. *Organometallics* **1982**, *1*, 1251.

[20] Denti, G.; Ghedini, M.; McCleverty, J. A.; Adams, H.; Bailey, N. A. *Transition Met. Chem.* **1982**, *7*, 222.

fashion, and the Mo–N bond lengths (2.172 (5), 2.134 (6), 2.128 (6) Å) are in reasonable agreement with those extant in [{HB(Me$_2$pz)$_3$}Mo(NO)(NCCH$_3$)$_2$]PF$_6$ (2.139 (9), 2.145 (9) Å). Interestingly, the acetonitrile ligand which is trans to the nitrosyl ligand in 1 exhibits a longer Mo–N bond (2.172 (5) Å) than the other two acetonitrile ligands, a feature which is reflective of its less successful competition for the available electron density on the metal center with the strongly electron-withdrawing trans NO group.

[Cp*Mo(NO)X(NCCH$_3$)$_2$]PF$_6$ (X = I, Br, Cl), Complexes 2, 4, and 6. Curiously, treatment of the bromo and chloro analogues, Cp*Mo(NO)X$_2$ (X = Br, Cl), with 1 equiv of NOPF$_6$ in CH$_3$CN under the same experimental conditions as for the iodo complex described in the previous section does not afford a dicationic product. Rather, these reactions produce monocationic organometallic complexes, i.e.

$$\text{Cp*Mo(NO)X}_2 \text{ in CH}_3\text{CN} \xrightarrow{\text{NO}^+} \underset{\substack{\mathbf{4},\ \text{X = Br} \\ \mathbf{6},\ \text{X = Cl}}}{[\text{Cp*Mo(NO)X(NCCH}_3)_2]\text{PF}_6} \quad (5)$$

The iodo analogue cannot be synthesized by this route, but it may be obtained, albeit in moderate yield, by treatment of Cp*Mo(NO)I$_2$ with 1 equiv of AgPF$_6$ in CH$_3$CN, i.e.

$$\text{Cp*Mo(NO)I}_2 \text{ in CH}_3\text{CN} \xrightarrow[\text{-AgI}]{\text{Ag}^+} \underset{\mathbf{2}}{[\text{Cp*Mo(NO)I(NCCH}_3)_2]\text{PF}_6} \quad (6)$$

In their pure forms, the three complexes 2, 4, and 6 are thermally stable, dark yellow to orange solids that can be handled in air for short periods of time with no noticeable decomposition occurring. If they are obtained in an impure form, they are prone to undergo decomposition to light brown oils when exposed to air. The complexes have similar solubility properties to those described for 1 above. Thus, they are soluble in polar organic solvents to give air-sensitive, light orange solutions.

IR spectra of 2, 4, and 6 as Nujol mulls display strong absorptions in the region 1668–1686 cm^{-1} (Table II) attributable to the terminal nitrosyl ligands. Again, these ν_{NO} values are shifted to higher frequencies than those exhibited by their neutral dihalo nitrosyl precursors. An interesting feature is that these nitrosyl stretching frequencies decrease in the order I > Br > Cl, i.e., opposite to that expected on the basis of the increasing electronegativity of the halide ligands. The exact reason for this opposite trend is not readily apparent, but it may be noted that a similar trend also occurs for the series of complexes CpW(NO)$_2$X (X = I, Br, Cl).[21]

In addition to the nitrosyl bands, weak absorptions attributable to the coordinated CH$_3$CN ligands are evident in the region 2322–2295 cm^{-1} in the Nujol mull IR spectra of 2, 4, and 6. By analogy to the structurally characterized cation in complex 1 (vide supra), the CH$_3$CN ligands in the organometallic cations of 2, 4, and 6 are probably coordinated to the metal centers via their N atoms in a linear fashion. The ^{1}H NMR spectra of these complexes also exhibit the expected resonances for the coordinated CH$_3$CN as well as the Cp* ligands (Table III). The chemical shifts of the Cp* proton resonances in the NMR spectra are in close agreement to those observed for the well-known complexes [Cp*Mo(CO)$_2$L$_2$][PF$_6$] (L = nitriles or phosphines).[22] Unlike the positions of the ν_{NO} bands in the IR spectra, the chemical shifts of the Cp* proton resonances in the NMR spectra do not exhibit any trends with respect to the halide ligands. The organometallic cations in complex 2, 4, and 6 probably possess the familiar four-legged piano stool molecular structures, but further discussion of their molecular geometries is deferred until the properties of several related complexes are first considered.

At this point an interesting comparison can be made between Cp*Mo(NO)I$_2$ and the closely related {HB(Me$_2$pz)$_3$}Mo(NO)I$_2$ with respect to their reactivity with AgPF$_6$ in CH$_3$CN. When {HB(Me$_2$pz)$_3$}Mo(NO)I$_2$ is treated with 1 equiv of AgPF$_6$ in CH$_3$CN, the paramagnetic product [{HB(Me$_2$pz)$_3$}Mo(NO)(NCCH$_3$)$_2$]PF$_6$ is obtained.[20] The same product is also obtained when 2 equiv of AgPF$_6$ is used. In contrast, when Cp*Mo(NO)I$_2$ is treated with 1 equiv of AgPF$_6$ in CH$_3$CN, complex 2 containing an organometallic monocation is obtained. However, when 2 equiv of AgPF$_6$ is employed, the dicationic complex 1 is formed.

[CpMo(NO)X(NCCH$_3$)$_2$]BF$_4$ (X = Br, Cl), Complexes 3 and 5. In contrast to their Cp* analogues (considered in the previous section), treatment of CpMo(NO)X$_2$ (X = Br, Cl) with 1 equiv of NOPF$_6$ in CH$_3$CN affords the corresponding [CpMo(NO)X(NCCH$_3$)$_2$]PF$_6$ salts only in very low yields (<5%). These low isolated yields are probably due to several factors. First, the long reaction times involved (4–5 h) may allow partial thermal decomposition of the cationic products. Second, in addition to the products of interest, many other nitrosyl-containing species (detectable by IR spectroscopy during the course of the reactions) are also formed during the reactions, thereby making the final isolation of the desired cationic complexes difficult. Third, the final cationic products are often contaminated with unreacted starting materials, thereby requiring repeated fractional crystallizations in the purification procedure which, in turn, lower the yields of the isolated salts. We have subsequently discovered that the [CpMo(NO)X(NCCH$_3$)$_2$]BF$_4$ (X = Br, Cl) complexes are obtainable in much higher yields by the treatment of the CpMo(NO)X$_2$ precursors with 1 equiv of a Ag$^+$ salt in CH$_3$CN, i.e.

$$\text{CpMo(NO)X}_2 + \text{AgBF}_4 \xrightarrow[\text{-AgX}]{\text{CH}_3\text{CN}} \underset{\substack{\mathbf{3},\ \text{X = Br} \\ \mathbf{5},\ \text{X = Cl}}}{[\text{CpMo(NO)X(NCCH}_3)_2]\text{BF}_4} \quad (7)$$

The physical properties of the new complexes 3 and 5 are quite similar to those exhibited by their Cp* analogues (Tables I–III). Their IR spectra as Nujol mulls display nitrosyl absorptions in the region 1709–1705 cm^{-1} which are approximately 20–35 cm^{-1} higher in energy than those exhibited by their Cp* analogues. This fact is simply a manifestation of the better electron-donating abilities of the Cp* ligand as compared to the Cp ligand. In addition, the ν_{CN} bands due to the coordinated CH$_3$CN ligands are also evident in the 2326–2299-cm^{-1} region of their IR spectra.

The solid-state molecular structure of complex 5 is shown in Figure 2, and selected intramolecular dimensions are presented in Table VI. The crystal structure of complex 5 involves the normal packing of discrete [CpMo(NO)Cl(NCCH$_3$)$_2$]$^+$ cations and BF$_4^-$ anions, the cation possessing the familiar four-legged piano stool molecular geometry. As for the other structures determined during this study, the anion exhibits fairly large thermal motion, the B–F bonds being apparently shortened as a result of thermal libration. In general, the structural parameters

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about the Mo atom in the cation exhibit normal values, and some comparisons with the corresponding values observed for related cationic Mo complexes can be made. For instance, the distance of the Mo atom from the plane of the Cp ring (2.032 (5) Å) in **5** is slightly longer than that found for [$Cp_2MoI(NCCH_3)$]PF_6 (1.986, 1.965 Å).[23] The Mo–Cl distance (2.416 (1) Å) in **5** is slightly shorter than those observed (ca. 2.44 Å) in other molybdenum complexes[24,25] but is indicative of the existence of a metal–chlorine single bond. The Mo–NO bond (1.790 (4) Å) is shorter and the N–O bond (1.183 (5) Å) in **5** is longer than the corresponding bond lengths in complex **1**. The MoNO group is also essentially linear in **5** (the Mo–N–O angle being 169.8 (4)°), although it is just slightly more bent than that in complex **1**. Again, the two trans CH_3CN ligands are N-bonded to the Mo center in a linear MoN≡CCH_3 fashion, the Mo–N bond lengths (2.160 (3), 2.141 (3) Å) being comparable to those in **1**. In closing, it may be noted that the closely related [$CpMo(NO)I(PMe_3)_2$]$^+$ complex cation has also been formulated as having trans PMe_3 ligands in the solid state.[26]

[$CpW(NO)I(NCCH_3)_2$]PF_6, Complex 7, and [$Cp^*W(NO)I(NCCH_3)_2$]BF_4, Complex 8. We had previously established that the Cp′W(NO)I_2 complexes exhibit chemical behavior different from that of their molybdenum congeners under reducing conditions.[27] Hence, for completeness, we decided to extend the current study with potential oxidizing agents to encompass some of the tungsten analogues of the dihalomolybdenum species described in the preceding paragraphs. What we have found is that under identical conditions the tungsten complexes do indeed behave similarly to their molybdenum congeners, but again careful attention must be paid to experimental details in order to obtain the desired organometallic cations. Thus, treatment of CpW(NO)I_2 with 1 equiv of $NOPF_6$ in CH_3CN affords the salt [$CpW(NO)I(NCCH_3)_2$]PF_6, complex **7**, i.e.

$$CpW(NO)I_2 \text{ in } CH_3CN \xrightarrow{NO^+} [CpW(NO)I(NCCH_3)_2]PF_6 \quad (8)$$

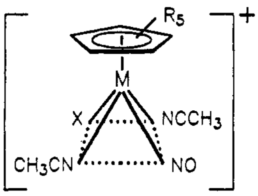
Unfortunately, attempts to extend reaction 8 to the Cp* analogue, Cp*W(NO)I_2, result in the formation of a mixture of several nitrosyl-containing products which are detectable by IR spectroscopy during the course of the reaction. The Cp* analogue of the organometallic cation in complex **7** is best obtained from the reaction between Cp*W(NO)I_2 and $AgBF_4$, i.e.

$$Cp^*W(NO)I_2 + AgBF_4 \xrightarrow[-AgI]{CH_3CN} [Cp^*W(NO)I(NCCH_3)_2]BF_4 \quad (9)$$

which affords the desired salt, [$Cp^*W(NO)I(NCCH_3)_2$]BF_4, complex **8**, in 72% isolated yield.

As pure solids, compounds **7** and **8** are slightly more air-sensitive than are their molybdenum congeners, but they can still be handled in air for short periods of time with no noticeable decomposition occurring. Their solubility properties are similar to those of their Mo analogues, although again the tungsten species are more air-sensitive in solutions. As expected, the IR spectra of complexes **7** and **8** exhibit ν_{NO}'s in the region 1686–1653 cm^{-1} attributable to the terminal nitrosyl ligands and weak ν_{CN}'s in the region 2324–2299 cm^{-1} due to the coordinated acetonitrile ligands. A comparison of the nitrosyl-stretching frequencies of [$Cp^*W(NO)I(NCCH_3)_2$]$^+$ with those of its Mo congener reveals that the ν_{NO} of the W complex is approximately 30 cm^{-1} lower in energy than that of the Mo complex. This trend is similar to that previously observed for the [$CpM(NO)I(PMe_3)_2$]$^+$ complexes (M = Mo, ν_{NO} 1668 cm^{-1}; M = W, ν_{NO} 1645 cm^{-1}).[26] The ^{1}H NMR spectra of complexes **7** and **8** exhibit the expected resonances for the coordinated CH_3CN ligands as well as the Cp or Cp* groups (Table III).

Probable Molecular Structures of the Monocationic Complexes. By analogy to complex **5**, the rest of the [$Cp'M(NO)X(NCCH_3)_2$]$^+$ cationic complexes described in this work probably possess four-legged piano stool molecular geometries in the solid state with the CH_3CN ligands trans to each other, i.e.



This view is substantiated by the similarities of the spectroscopic properties of complexes **2**–**4** and **6**–**8** to those of the structurally characterized complex **5**. In solutions, however, these complexes may well be in rapid equilibrium with their cis isomers.

Proposed Mechanism for the Reaction of Cp′M(NO)X_2 with [NO]$^+$. In all the transformations which result in the conversion of the neutral dihalo nitrosyl complexes, Cp′M(NO)X_2, to the cationic products, [$Cp'M(NO)X(NCCH_3)_2$]$^+$ or [$Cp'M(NO)(NCCH_3)_3$]$^{2+}$, no change in the formal oxidation state of the metal center occurs. Indeed, when the reagent is an Ag^+ salt, these reactions may be viewed as proceeding via initial halide abstraction followed by subsequent incorporation of the requisite number of acetonitrile molecules into the metal's coordination sphere. However, when the reagent is a nitrosonium salt, the situation is not so straightforward. While the exact mechanisms for these latter reactions remain to be established, a plausible reaction pathway for the formation of [$Cp'Mo(NO)X(NCCH_3)_2$]$^+$ by the reactions of NO^+ with Cp′Mo(NO)X_2 in CH_3CN is

$$\begin{tikzcd}
{[Cp'Mo(NO)X_2(NCCH_3)]} \arrow[d, "+NO^+"', "-NO^\bullet"] \\
{[Cp'Mo(NO)X_2(NCCH_3)]^{\bullet+}} \arrow[d, "-X^\bullet"] \\
{\text{"}[Cp'Mo(NO)X(NCCH_3)]^+\text{"}} \arrow[d, "+CH_3CN"'] \\
{[Cp'Mo(NO)X_2(NCCH_3)_2]^+}
\end{tikzcd}$$

In its reactions with transition-metal compounds, NO^+ may behave as a nitrosylating agent or as a 1-electron oxidant.[28] The 16-electron dihalo nitrosyl complexes, Cp′Mo(NO)X_2, in CH_3CN solution are probably stabilized by the coordination of a CH_3CN molecule to the Mo center. As

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summarized above, the initial step of the reaction may well involve the oxidation by NO^+ of the 18-electron $Cp'Mo(NO)X_2(NCCH_3)$ complex to the 17-electron radical cation, $[Cp'M(NO)X_2(NCCH_3)]^+$, the oxidant being reduced to $NO^\bullet$. The postulated radical-cation intermediate is consistent with our observations that the reactions of the perhydro complexes, $CpMo(NO)X_2$, with NO^+ require a longer time to go to completion than do those of the permethylated analogues, $Cp^*Mo(NO)X_2$. This observation is presumably a reflection of the fact that the ease of oxidation of a transition-metal complex generally increases with the increase in electron density on the metal center. The transient formation of the 17-valence-electron metal center could labilize the halide ligand which would be lost as $X^\bullet$ and then be trapped by $NO^\bullet$ to form XNO, the latter being well-known species.[29] The resulting 16-electron intermediate $[Cp'Mo(NO)X(NCCH_3)]^+$ could then be further stabilized by the incorporation of another molecule of CH_3CN to yield the final 18-electron product, $[Cp'Mo(NO)X(NCCH_3)_2]^+$.

Synthesis and Characterization of the Paramagnetic Complex 9, $[CpCr(NO)(NCCH_3)_2]PF_6$. The direct extension of the molybdenum and tungsten chemistry presented earlier in this paper to encompass chromium is thwarted by the fact that halo complexes of the type $CpCr(NO)X_2$ remain unknown. Indeed, the most closely related chromium complex is $[CpCr(NO)I]_2$, and so we decided to use it as the synthetic precursor. Not surprisingly, the product resulting from the treatment of $[CpCr(NO)I]_2$ with a silver(I) salt in CH_3CN does not resemble any of those produced by the Mo and W dihalo nitrosyl complexes (vide supra). Instead, the reaction portrayed in eq 10 occurs, the new complex **9** being isolable

$$[\mathrm{CpCr(NO)I}]_2 + 2\mathrm{AgPF_6} \xrightarrow[-2\mathrm{AgI}]{\mathrm{CH_3CN}} \underset{\mathbf{9}}{2[\mathrm{CpCr(NO)(NCCH_3)_2}]\mathrm{PF_6}} \tag{10}$$

in 48% yield by the addition of Et_2O to the filtrate of the final reaction mixture. Complex **9** is a paramagnetic green solid that can be handled in air for several hours without any noticeable decomposition. It is soluble in CH_3CN CH_3NO_2, and THF and is sparingly soluble in CH_2Cl_2 to yield bright green air- and moisture-sensitive solutions. Its IR spectrum as a Nujol mull (Table II) exhibits features diagnostic of the presence of both the nitrosyl and acetonitrile ligands. Its ESR spectrum as a DMF solution at room temperature displays a broad three-line pattern ($g = 1.984$) with approximately equal peak intensities. This pattern results from the hyperfine coupling of the unpaired electron with ^{14}N of the NO ligand ($a(^{14}N) = 5.21$ G) and indicates that the unpaired electron density in the radical cation is primarily localized on the nitrosyl group.

The solid-state molecular structure of complex **9** is shown in Figure 3, and selected intramolecular dimensions are summarized in Table VI. The chromium cation of complex **9** is monomeric with a three-legged piano stool molecular geometry. Within the CrNO linkage in complex **9**, the Cr–N distance (1.685 (6) Å) and the N–O distance (1.174 (7) Å) are virtually identical to the same bond distances found for $(\eta^5\text{-}C_{13}H_9)Cr(CO)_2(NO)$ (1.687, 1.169 Å).[30] As for the other organometallic cations characterized crystallographically during this study, the metal–NO link is essentially linear and the two acetonitrile ligands are N-bonded in a linear fastion to the metal center. The latter Cr–N bond lengths (2.025 (16), 1.993 (12) Å) are in reasonable agreement with the previously determined structures of cationic Cr complexes having N-bonded acetonitrile ligands.[31]

The cation in complex **9** is one of only a few such cationic complexes to have been reported to date. The only other known examples of 17-valence-electron cations belonging to this class of compounds are the $[CpCr(NO)(L\text{–}L)]^+$ species (L–L represents the bidentate ligands bpy and phen) which are preparable by the thermolysis of $[CpCr(NO)_2(NCCH_3)]^+$ salts in the presence of L–L.[32]

Epilogue

Although cationic organometallic complexes containing the $Cp'M(NO)_2$ dinitrosyl fragments are frequently encountered in group 6 nitrosyl chemistry, cationic complexes containing the mononitrosyl fragments, $Cp'M(NO)$, are not as common. Complexes **1**–**9** can be formally viewed as organometallic Lewis acids, $[Cp'M(NO)X]^+$, $[CpCr(NO)]^+$, or $[Cp^*Mo(NO)]^{2+}$, stabilized by the coordination of weakly basic CH_3CN ligands. These cationic complexes constitute a class of isolable group 6 transition-metal nitrosyl complexes containing the $Cp'M(NO)$ fragments. Some of the monocationic complexes **2**–**9** isolated in this work have some precedents int he chemical literature (vide supra), but no dicationic compound containing a $Cp'M(NO)$ fragment has yet been reported. In other words, complex **1**, $[Cp^*Mo(NO)(NCCH_3)_3][PF_6]_2$, contains an unprecedented organometallic nitrosyl cation.

There have been several reports in the literature concerning the formation and synthetic applications of transition-metal acetonitrile complexes.[33,34] For instance, Sen and co-workers have shown that the complexes $[M(NO)_2(NCCH_3)_4]^{2+}$ (M = Mo, W) and $[Pd(NCCH_3)_4]^{2+}$ can induce the oligomerization of a wide range of olefins under mild conditions.[33b] This activity is attributed to the lability of the CH_3CN ligands in solution, thereby allowing easy solvent–substrate exchange in the metal's coordination sphere and further substrate activation which is induced by the presence of the electrophilic metal center. In addition, the extensive chemistry exhibited by the cationic carbonyl complexes $[(\eta^5\text{-}C_5R_5)Mo(CO)_2(NCCH_3)_2]^+$ and $[(\eta^5\text{-}C_5R_5)M(CO)_{3-n}(NCCH_3)_n]^+$ (R = H, Me; M = Fe, Ru; $n = 1,2$) is well documented.[34] Furthermore, the gegenions PF_6^- or BF_4^- in complexes **1**–**9** are noncoordinating (or at most weakly coordinating), a property which means that they should be replaceable by other potential ligands under mild conditions. Given the chemistry exhibited by other cationic transition-metal acetonitrile complexes,[35] it is not unreasonable to suggest that the organometallic nitrosyl cations in complexes **1**–**9** should, in principle, be utilizable in organic synthesis and serve as useful precursors to a variety of new types of nitrosyl complexes. The characteristic chemistry of these cationic complexes is currently being investigated.

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Supplementary Material Available: Tables of anisotropic thermal parameters for the non-hydrogen atoms, positional and thermal parameters for the hydrogen atoms, and bond lengths, bond angles, and torsion angles involving non-hydrogen atoms for $[Cp^*Mo(NO)(NCCH_3)_3][PF_6]_2$ (**1**), $[CpMo(NO)Cl(NCCH_3)_2]BF_4$ (**5**), and $[CpCr(NO)(NCCH_3)_2]PF_6$ (**9**) and stereoviews of the packing diagrams (21 pages); listings of observed and calculated structure factors for all three complexes (56 pages). Ordering information is given on any current masthead page.

Equilibrium Studies of the Displacement of $\eta^1(S)$-Thiophenes (Th) from $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-Th})^+$

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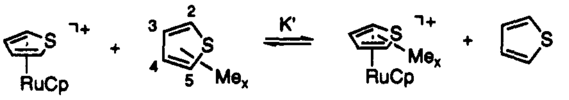
The reactions of $Cp(CO)(PPh_3)RuCl$ ($Cp = \eta^5\text{-}C_5H_5$) with Ag^+ and thiophenes (Th) produce the stable sulfur-bound (η^1(S)) thiophene complexes $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-Th})^+$ (Th = T, 2-MeT, 3-MeT, 2,5-Me_2T, Me_4T, BT, and DBT). Equilibrium constants (K') for the displacement of thiophene (T) by methyl-substituted thiophenes, benzo[*b*]thiophene (BT), and dibenzothiophene (DBT), $Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-T})^+ + Th' \rightleftarrows Cp(CO)(PPh_3)Ru(\eta^1(S)\text{-Th}')^+ + T$, increase in the following order: T (1) < 2,5-Me_2T (2.76) < 2-MeT (4.11) < 3-MeT (6.30) < BT (29.9) < Me_4T (57.4) < DBT (74.1). In general, methyl groups on thiophene increase K', but α-methyl groups reduce the stabilities of complexes with 2-MeT, 2,5-Me_2T, and Me_4T ligands due to a steric interaction with the PPh_3 group. The ligands tetrahydrothiophene (THT) and MeCN have K' values ($>7.1 \times 10^6$) which are much higher than any of the thiophenes, while MeI (K' = 2.0) is a slightly better ligand than T. An X-ray structure determination of $[Cp(CO)(PPh_3)Ru(2\text{-MeT})]BF_4$ is also reported.

Introduction

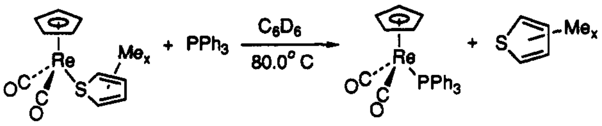
An important step in the mechanism(s) of thiophene (T) hydrodesulfurization (HDS) on heterogeneous catalysts is its adsorption to a metal site on the catalyst surface. Results of heterogeneous studies[2] indicate that methyl-substituted thiophenes bind more strongly to a Co–Mo/Al_2O_3 catalyst than thiophene itself; the adsorption equilibrium constants (in parentheses) decrease in the order 2,5-dimethylthiophene (2,5-Me_2T) (2.5) > 3-methylthiophene (3-MeT) (1.7) ≈ 2-methylthiophene (2-MeT) (1.6) > T (1.0). The same trend is observed for η^5-thiophene binding in the complexes $CpRu(\eta^5\text{-Th})^+$;[3] equilibrium constants (K') for eq 1 decrease with different



(1)

methyl-substituted thiophenes Th′ in the order Me_4T > 2,5-Me_2T > 3-MeT > 2-MeT > T (where Me_4T is tetramethylthiophene). These similar trends are consistent with η^5-binding of thiophene on the catalyst surface. The well-known reactivity[4] of η^5-thiophene in its metal complexes also supports such an adsorption mode on HDS catalysts.

The other common mode of thiophene coordination in transition-metal complexes is η^1(S) through the sulfur.[5] Complexes exhibiting this mode of thiophene binding are as follows: $Ru(NH_3)_5(T)^{2+}$,[6] $Cp(CO)_2Fe(T)^+$,[7] $CpFe(NCMe)_2(2,5\text{-}Me_2T)^+$,[8] $W(CO)_3(PCy_3)_2(T)$,[9] $(C_5H_4CH_2C_4H_3S)Ru(PPh_3)_2{}^+$,[10] $Cp^*(CO)_2Re(T)$,[11] $MX_2(L')$ (M = Pd, X = Cl, Br, I, SCN; M = Pt, X = Cl),[12a] $[CuCl_2(L')]_2$,[12b] $Pd(\eta^3\text{-allyl})(L')$[12c] (L′ = 2,5,8-trithia[9]-(2,5)thiophenophane), $[RuClL_2]BF_4$[13] (L = 6-(2-thienyl)-2,2′-bipyridine), and $Cp(CO)_2Fe(2,5\text{-}Me_2T)^+$.[14] Kinetic studies[15] of the replacement (eq 2) of methyl-sub-



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