petroleum ether; yield 87%. When $NaBH_4$ (ethanol) or $LiHBEt_3$ (1 M THF) were employed as reducing agents, the isolated crude product contained **4** together with some amount (20–30%) of (triphos)RhH(S_2CO) (**5**). Compound **4** was separated from **5** by recrystallization from CH_2Cl_2/ethanol. When the reduction of **1** to **4** was achieved by using $(C_5H_5)_2Co$ (CNMe) or $(NP_3)Ni$ (THF), the compounds $[(C_5H_5)_2Co][BPh_4]$ and $[(NP_3)Ni][BPh_4]$ were also isolated from the reaction mixture, respectively. Anal. Calcd for $C_{42}H_{39}OP_3RhS_2$: C, 61.54; H, 4.79; Rh, 12.55. Found: C, 61.46; H, 4.78; Rh, 12.31.

(triphos)RhH(S_2CO) (5). Addition of BH_3·THF (1 M THF) (0.5 mL, 0.5 mmol) to a solution of **1** (0.34 g, 0.3 mmol) in THF (20 mL) caused an immediate color change from red to yellow. On addition of ethanol (5 mL) white crystals of **5** precipitated within a few minutes, which were filtered off and washed with ethanol and petroleum ether; yield 92%. Anal. Calcd for $C_{42}H_{40}OP_3RhS_2$: C, 61.46; H, 4.91; Rh, 12.53. Found: C, 61.29; H, 4.82; Rh, 12.38.

Reaction of 1 with HSO_3CF_3 (or $MeSO_3CF_3$). Neat HSO_3CF_3 (or $MeSO_3CF_3$) (0.3 mmol) was syringed into a magnetically stirred THF (20 mL) solution of **1** (0.34 g, 0.3 mmol) in a Schlenk flask equipped with a rubber septum. After 30 min the gaseous phase was analyzed by using a gas chromatograph, which revealed the presence of H_2S, Me_2S, CO, and COS. The resulting red-brown solution, treated with $NaBPh_4$ (0.17 g, 0.5 mmol) in ethanol (20 mL), gave brown crystals of $[(triphos)Rh(\mu\text{-}S)_2Rh(triphos)][BPh_4]_2$ (**8**); yield 78%.

(triphos)RhPh(S_2CO) (9). A mixture of **1** (0.34 g, 0.3 mmol) and $(PPh_3)_3CuClO_4$ (0.28 g, 0.3 mmol) in THF (20 mL) was stirred at room temperature for 1 h. The solution color changed from red to yellow-orange, and pale yellow crystals of **9** precipitated. They were separated by filtration (yield 55%) from the mother liquor, which gave on addition of ethanol (20 mL) a precipitate containing further **9** and the starting copper complex. Anal. Calcd for $C_{48}H_{44}OP_3RhS_2$: C, 64.28; H, 4.94; Rh, 11.47. Found: C, 63.99; H, 4.88; Rh, 11.32.

Reaction of 9 with HSO_3CF_3. Neat HSO_3CF_3 (0.3 mmol) was syringed into a magnetically stirred solution of **9** (0.27 g, 0.3 mmol) in CH_2Cl_2 (20 mL) in a Schlenk flask equipped with a rubber septum. After 10 min the GC analysis of the gaseous and the liquid phase showed the presence of COS and benzene, respectively. The resulting red-brown solution, treated with $NaBPh_4$ (0.17 g, 0.5 mmol) in ethanol (20 mL), gave brown crystals of **8**; yield 85%.

Reaction of 9 with H_2. Hydrogen was bubbled for 1 h through a suspension of **9** (0.27 g, 0.3 mmol) in THF (20 mL), during which the starting solid dissolved and new crystals of **5** precipitated in 91% yield. The GC analysis of the reaction mixture showed the formation of benzene.

[(triphos)Rh(S_2CS)][BPh_4] (10). Neat CS_2 (0.06 mL, 1 mmol) was syringed into a solution of $[1][BPh_4]$ (1.14 g, 1 mmol) in 30 mL of CH_2Cl_2 in a Schlenk flask equipped with a rubber septum. There was an immediate color change from red-brown to brilliant red and, simultaneously, COS evolution as determined by the GC analysis of the gaseous phase. Addition of ethanol (40 mL) gave red crystals of **10**, which were collected by filtration and washed with ethanol and petroleum ether; yield 95%. Anal. Calcd for $C_{66}H_{59}BP_3RhS_3$: C, 68.63; H, 5.14; Rh, 8.91; S, 8.32. Found: C, 68.45; H, 5.07; Rh, 8.73; S, 8.21.

[(triphos)Rh(S_2CNR)][BPh_4] (R = Ph (11), Et (12)). Dark violet crystals of **11** and **12** were obtained in 95% yield by following the same procedure as above but replacing CS_2 with SCNR (R = Ph, Et). Alternatively, **10** was treated in CH_2Cl_2 with a 2-fold excess of SCNR and worked up as above. The interconversion between **11** and **12** was simply achieved by adding an excess of SCNEt or SCNPh to a CH_2Cl_2 solution of **11** or **12**, respectively. The formation of COS, CS_2, and SCNR in the course of the reactions was determined by GC. Anal. Calcd for $C_{72}H_{64}BNP_3RhS_2$ (**11**): C, 71.23; H, 5.31; N, 1.15; Rh, 8.47. Found: C, 71.04; H, 5.19; N, 1.01; Rh, 8.33. Anal. Calcd for $C_{72}H_{64}BNP_3RhS_2$ (**12**): C, 70.04; H, 5.53; N, 1.20; Rh, 8.82. Found: C, 69.87; H, 5.34; N, 1.12; Rh, 8.73.

Acknowledgment. Thanks are due to Aldo Traversi for technical assistance.

Registry No. $[1][BPh_4]$, 99955-64-3; **4**, 117896-52-3; **5**, 110637-36-0; **6**, 117896-54-5; **7**, 82590-72-5; **8**, 105139-43-3; **9**, 117896-53-4; **10**, 109637-03-8; **11**, 109637-05-0; **12**, 109637-07-2; **13**, 117896-57-8; LiMe, 917-54-4; LiPh, 591-51-5; $NaC_{10}H_8$, 3481-12-7; BH_3·THF, 14044-65-6; S_2CO^{2-}, 30981-29-4; HSO_3CF_3, 1493-13-6; $MeSO_3CF_3$, 333-27-7; $(PPh_3)_3CuClO_4$, 34010-81-6; BPh_4^-, 4358-26-3; CS_2, 75-15-0; SCNPh, 103-72-0; SCNEt, 542-85-8; [(triphos)Rh(S_2CO)][BPh_4], 97689-99-1; [(triphos)Rh(S_2CO)]$^-$, 117896-55-6; [(triphos)Co(S_2CO)]$^+$, 117896-56-7; CS_3^{2-}, 15644-49-2; $PhNCS_2^{2-}$, 117861-48-0; $EtNCS_2^{2-}$, 117861-49-1.

Supplementary Material Available: Figure 1S (X-band ESR spectra of (triphos)Rh(Se_2CO) in CH_2Cl_2 at 100 K (a) and 300 K (b)) and Figure 2S (experimental (a) (CD_2Cl_2, 298 K, 300 MHz, $MeSi_4$ reference) and computed (b) ^1H NMR spectra of (triphos)RhPh(S_2CO) in the interval between 6.7 and 6.4 ppm) (2 pages). Ordering information is given on any current masthead page.

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The Iron–Nitrato/Iron–Nitrosyl Couple in the Presence of Hexamethylphosphoric Triamide and Its Relevance to Oxygen Activation and Transfer. X-ray Structure of $Fe(NO_3)(Cl)_2(HMPA)_2$

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The nitrosyl dimer $[Fe(NO)_2(Cl)]_2$ (**1**) in the presence of hexamethylphosphoric triamide (HMPA) yields the unstable compound $Fe(NO)_2(Cl)(HMPA)$ (**2**), which gives through NO dissociation $Fe(NO)(Cl)_2(HMPA)\cdot{}^1/_2HMPA$ (**3**). Oxidation by oxygen (1 atm) of the Fe–NO moiety in **2**, **3**, or **1** in the presence of HMPA results in the formation of the nitrato—and not nitro—complexes $Fe(NO_3)(Cl)_2(HMPA)\cdot{}^1/_2HMPA$ (**4**), $Fe(NO_3)_2(Cl)(HMPA)\cdot{}^1/_2HMPA$ (**6**), $Fe(NO_3)_2(Cl)(HMPA)_2$ (**7**) and $Fe(NO_3)(Cl)_2(HMPA)_2$ (**8**). The molecular structure of **8** has been determined by X-ray diffraction. Crystal data (at -100 °C): monoclinic, space group $P2_1/c$, $a = 15.994$ (5) Å, $b = 10.172$ (3) Å, $c = 16.571$ (5) Å, $\beta = 104.7$ (1)°, $V = 2608$ Å^3, $Z = 4$, $R_w = 0.051$ for 3029 reflections with $I > 3.0\sigma(I)$. The nitrates **7** and **8** are capable of oxygen transfer to phosphines, thus regenerating the Fe–NO moiety. The nitrato complexes were found to be catalysts in the autoxidation of cyclohexene.

Introduction

There is a need for developing nonradical systems for oxidation and, in particular, for the epoxidation of olefins by molecular oxygen. A possible route consists of splitting the oxygen molecule on a ligand of a transition metal to form a complex with the ligand in the oxidized form; the oxygen of the oxidized ligand would then transfer to an organic substrate. This chemistry was first demonstrated for the nitro/nitrosyl redox couple.[1,2]

We have found[3] that the iron–nitrato–iron–nitrosyl couple could constitute a new alternative for the activation and transfer of molecular oxygen; the nitrosyl ligands in the dinitrosyliron dimers

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(1) Solar, J. P.; Mares, F.; Diamond, S. E. *Catal. Rev.—Sci. Eng.* **1985**, *27*, 1 and references therein.

(2) Andrews, M. A.; Chang, T. C. T.; Cheng, C. W. F. *Organometallics* **1985**, *4*, 268 and references therein.

(3) Tomi, F.; Li Kam Wah, H.; Postel, M. *New J. Chem.* **1988**, *12*, 289.

Table I. Elemental Analysis and IR Data for Compounds **3**–**8**

	anal. found (calcd), %						IR, cm^{-1} (KBr pellets)		
complex	C	H	N	Cl	Fe	P	$\nu(NO_3)$	$\nu(FeCl)$	$\nu(P{=}O)$
$Fe(NO)(Cl)_2(HMPA)\cdot{}^1/_2HMPA$ (**3**)				17.69 (16.66)	12.71 (13.12)	11.14 (10.92)		330 376	1190 1132
$Fe(NO_3)(Cl)_2(HMPA)\cdot{}^1/_2HMPA$ (**4**)	24.24 (23.63)	6.06 (5.95)	16.46 (16.84)	16.05 (15.50)	11.60 (12.21)	10.68 (10.15)	1528 1280 808	382	1188 1157
$Fe(Cl)_3(HMPA)\cdot{}^1/_2HMPA$ (**5**)	25.08 (25.07)	6.31 (6.31)	14.62 (14.63)	24.61 (24.60)				382 355 330	1190
$Fe(NO_3)_2(Cl)(HMPA)\cdot{}^1/_2HMPA$ (**6**)	22.33 (21.91)	5.62 (5.57)		7.32 (7.41)			1550 1524 1281	380	1188
$Fe(NO_3)_2(Cl)(HMPA)_2$ (**7**)	25.12 (25.15)	6.33 (6.19)	19.53 (19.44)	6.18 (5.66)	9.73 (9.88)	10.80 (10.57)	1510 1283 808	350	1190
$Fe(NO_3)(Cl)_2(HMPA)_2$ (**8**)	26.34 (26.15)	6.63 (6.67)	17.92 (17.92)	12.96 (12.47)	10.21 (10.21)	11.32 (11.27)	1510 1277 804	384 332	1190

$[Fe(NO)_2X]_2$ (X = Cl, I) are oxidized by molecular oxygen, in the presence of PPh_3 or $OPPh_3$, to nitrato and not nitro ligands, from which oxygen is then transferred to phosphines and olefins.

However, such oxidizable ligands as phosphines are not likely to produce long-lived active species; furthermore, the nitrosyl species in the couple was found to encounter side reactions leading to the termination of the catalytic cycle in this system. Hexamethylphosphoric triamide (HMPA), a nonoxidizable labile ligand, classically utilized in this field of activation of oxygen, seemed an appealing alternative. We report here that, in the presence of HMPA, the iron–nitrosyl moiety is, here again, oxidized by O_2 into iron–nitrato species, some of which are capable of transferring oxygen.

Experimental Section

All reagents and solvents were reagent grade. Solvents were purified by published procedures and stored under argon. HMPA was purchased from Aldrich and distilled under sodium. $AgNO_3$ and PPh_3 were purchased from Fluka and used without further purification. PPh_3 was checked periodically by IR spectroscopy to ensure the absence of $OPPh_3$. $[Fe(NO)_2(Cl)]_2$ was prepared according to the literature.[4] The preparations of the nitrosyl complexes were performed under an atmosphere of argon using Schlenk techniques. The analytical and infrared data are gathered in Table I.

IR spectra were obtained on a Bruker FT-IFS 45 spectrometer. Samples were prepared as KBr pellets or Nujol mulls. ESR spectra were recorded on a Bruker 200 SRC spectrometer equipped with a variable-temperature accessory. Samples were prepared in quartz tubes. Elemental analyses were performed by the Service Central d'Analyse of the CNRS. GLC/MS coupling was obtained on a RIBERMAG R 10 spectrometer associated with a Girdel 300 chromatograph equipped with a CP 5 25 m × 0.32 mm capillary column.

Caution! Hexamethylphosphoric triamide (HMPA) is a potential carcinogen; upon manipulation, breathing apparatus and gloves should be worn.

Preparation of $Fe(Cl)_3(HMPA)\cdot{}^1/_2HMPA$ (5). A solution of hexamethylphosphoric triamide (3.5 g, 19.53 mmol) in acetonitrile (25 mL) was added dropwise with stirring to a solution of anhydrous iron(III) chloride (1.57 g, 9.68 mmol) in 25 mL of acetonitrile. No obvious color change was noted. After 2 h, the yellow-orange solution was evaporated to dryness and the residue was washed with pentane and diethyl ether and dried under vacuum; yield 3.71 g, 89%. On very slow concentration of the acetonitrile solution, yellow crystals were obtained.

Preparation of $Fe(NO)(Cl)_2(HMPA)\cdot{}^1/_2HMPA$ (3) from the Chlorodinitrosyliron Dimer 1. A solution of 0.28 g of hexamethylphosphoric triamide (1.56 mmol) in 20 mL of diethyl ether was added to a solution of $[Fe(NO)_2(Cl)]_2$ (0.23 g, 0.76 mmol) in 20 mL of dichloromethane. The mixture was stirred at room temperature for 3 h. After filtration, the filtrate was evaporated to yield an oily black liquid. Washing several times with pentane gave 0.24 g of a gray powder, **2**, which was very unstable in the presence even of mere traces of air. IR (KBr, cm^{-1}): $\nu(NO)$ = 1761 (s), 1699 (s); $\nu(P{=}O)$ = 1190 (s), 1130 (s); $\nu(FeCl)$ = 353 (m). EPR (CH_2Cl_2, 143 K): g = 2.037 (single line).

A 0.20-g amount of **2** was dissolved in 5 mL of dichloromethane, and an equal volume of pentane was added. The solution was kept at 0 °C under argon. After ca. 12 h, green crystals of the product **3** (0.09 g, 45%) had formed at the interface, so they could easily be separated from the brown residue that deposited at the bottom of the vessel.

Preparation of $Fe(NO_3)(Cl)_2(HMPA)\cdot{}^1/_2HMPA$ (4). (a) From 3. Oxygen was bubbled through an acetonitrile solution (25 mL) of the green nitrosyl product **3** (0.30 g, 0.7 mmol) at room temperature for 15 min, resulting in an immediate color change to yellow. After the solution was evaporated to dryness and the residue was washed with 2 × 20 mL of pentane, the yellow powder was dried under vacuum; yield 0.28 g, 88%.

(b) By Direct Preparation. A solution of silver nitrate (0.099 g, 0.583 mmol) in acetonitrile (25 mL) was added dropwise to a solution of **5** (0.25 g, 0.58 mmol) at room temperature. Instantaneous formation of a white precipitate of AgCl resulted; the suspension was stirred for 1 h before filtration and evaporation to dryness. The yellow residue was recrystallized in a 1:1 CH_2Cl_2–pentane mixture; yield 0.24 g, 91%.

Preparation of $Fe(NO_3)_2(Cl)(HMPA)\cdot{}^1/_2HMPA$ (6). (a) From the Chlorodinitrosyliron Dimer 1. The chlorodinitrosyliron dimer $[Fe(NO)_2(Cl)]_2$ (**1**; 2.42 g, 7.997 mmol) was dissolved in acetonitrile (100 mL), and hexamethylphosphoric triamide (2.93 g, 16.35 mmol) was added over 10 min with stirring. The solution was bubbled with oxygen gas for 1 h, resulting in evolution of brown fumes and in an immediate color change from black to orange-yellow. The reaction mixture was filtered, and the solvent was evaporated. The orange oily residue was washed with 2 × 50 mL of pentane and 2 × 50 mL of diethyl ether and dried under vacuum; yield 3.47 g, 45%.

(b) By Direct Preparation. A solution of silver nitrate (0.22 g, 1.29 mmole in acetonitrile (25 mL) was added dropwise to a solution of **5** (0.31 g, 0.64 mmol) in acetonitrile (25 mL) at room temperature. Instantaneous formation of a white precipitate of AgCl resulted. The suspension was stirred for 1 h before filtration and evaporation to dryness. The yellow residue obtained was washed with 2 × 20 mL of pentane and 2 × 20 mL of diethyl ether and dried under vacuum; yield 0.49 g, 80%.

Preparation of $Fe(NO_3)_2(Cl)(HMPA)_2$ (7). (a) From the Chlorodinitrosyliron Dimer 1. The chlorodinitrosyliron dimer $[Fe(NO)_2(Cl)]_2$ (**1**; 0.78 g, 2.577 mmol) was dissolved in acetonitrile (50 mL), and hexamethylphosphoric triamide (2.01 g, 11.22 mmol) was added over 10 min with stirring. The solution was bubbled with oxygen gas for 1 h, resulting in an immediate color change from black to yellow; the reaction mixture was filtered, and the solvent was evaporated from the filtrate. The yellow residue was washed with 2 × 20 mL of pentane and 2 × 20 mL of diethyl ether and dried under vacuum; yield 2.7 g, 91%. EPR (CH_2Cl_2, at ambient and low temperatures): g = 2.016 (single line).

(b) By Direct Preparation. A solution of silver nitrate (0.7781 g, 4.580 mmol) in acetonitrile (25 mL) was added dropwise to a solution of anhydrous iron(III) chloride (0.37 g, 2.28 mmol) and hexamethylphosphoric triamide (0.84 g, 4.69 mmol) in acetonitrile (50 mL). A color change from orange to yellow and formation of a white solid (AgCl) occurred immediately. The suspension was stirred for 1 h and let stand overnight. After filtration, the solution was evaporated to dryness. The yellow residue was washed with 2 × 20 mL of pentane and 2 × 20 mL of diethyl ether and dried under vacuum; yield 1.25 g, 95%. EPR (CH_2Cl_2, at ambient and low temperatures): g = 2.016 (single line).

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[4] Ballivet-Tkatchenko, D.; Billard, C.; Revillon, A. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1697.

Scheme I

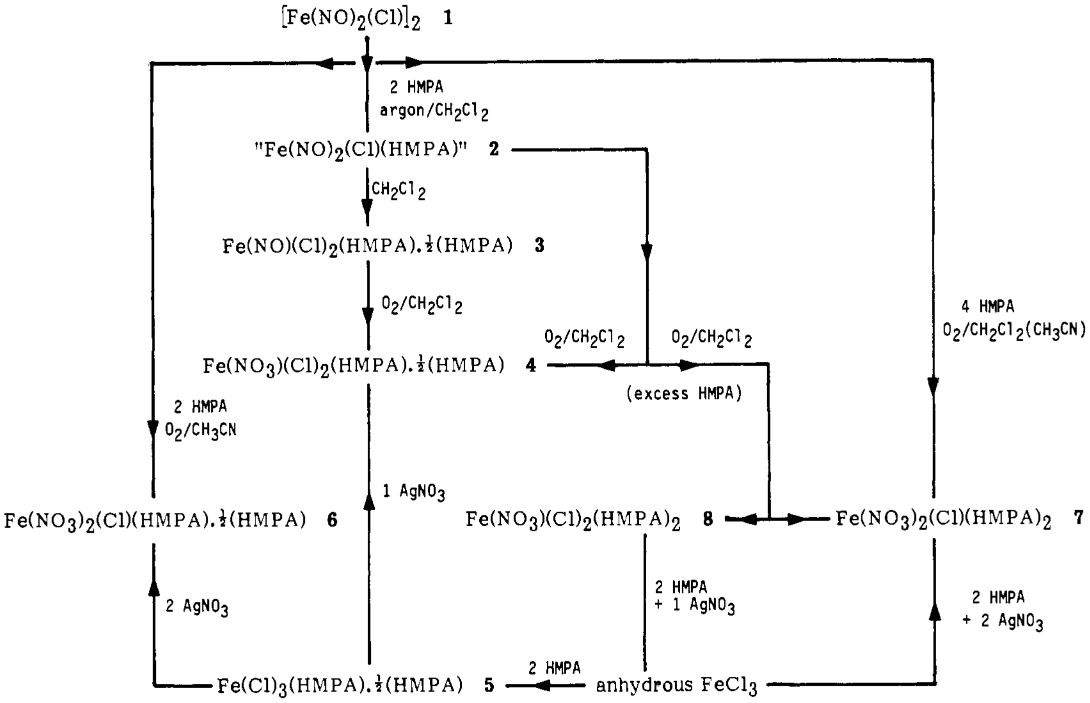

Table II. Crystallographic Data for **8**

$FeCl_2P_2O_5N_7C_{12}H_{36}$	fw: 547.2
$a = 15.994$ (5) Å	space group: $P2_1/c$
$b = 10.172$ (3) Å	$T = -100$ °C
$c = 16.571$ (5) Å	$\lambda = 0.71069$ Å
$\beta = 104.7$ (1)°	$\rho_{obsd} = 1.395$ g cm^{-3}, $\rho_{calcd} = 1.393$ g cm^{-3}
$V = 2608$ Å^3	$\mu = 9.37$ cm^{-1}
$Z = 4$	$R = 0.049$
	$R_w = 0.051$

Preparation of $Fe(NO_3)(Cl)_2(HMPA)_2$ (8). (a) From 2. Oxygen was bubbled through a dichloromethane solution (25 mL) of the gray nitrosyl product **2** (0.20 g, 0.6 mmol) at room temperature together with an excess of HMPA (0.107 g, 0.6 mmol) for 15 min, resulting in an immediate change from black to yellow. By slow evaporation of the dichloromethane solution, which is shown by IR spectroscopy to contain both **7** and **8**, yellow parallelepiped-shaped crystals of $Fe(NO_3)(Cl)_2(HMPA)_2$ were obtained (0.08 g, 25%).

(b) By Direct Preparation. A solution of silver nitrate (0.68 g, 4.01 mmol) in acetonitrile (25 mL) was added dropwise to a solution of anhydrous iron(III) chloride (0.65 g, 8.09 mmol) and hexamethylphosphoric triamide (1.45 g, 8.09 mmol) in acetonitrile (25 mL). A color change from orange to yellow and formation of a white precipitate (AgCl) occurred immediately. The solution was stirred for 1 h and let stand overnight. After filtration, the solution was evaporated to dryness. The yellow residue was washed with 2 × 20 mL of diethyl ether and dried under vacuum; yield 1.65 g, 75%. EPR (CH_2Cl_2, at ambient and low temperatures): $g = 2.016$ (single line).

General Procedure for the Oxidation Tests. To a solution of the iron complex to be tested was added about 100 equiv of cyclohexene together with *n*-octane as an internal standard for the GC measurements. The resulting solution was stirred under an atmosphere of oxygen and the formation of oxidation products monitored by GLC analysis of aliquot samples. The oxygenated products were identified by GLC-MS coupling and comparison of the mass spectra with those of authentic samples.

Crystal Structure of $Fe(NO_3)(Cl)_2(HMPA)_2$ (8). Single yellow parallelepiped-shaped crystals suitable for X-ray studies were obtained by slow evaporation of a saturated dichloromethane solution of the crude product resulting from oxygenation of **2** at room temperature. These crystals are monoclinic and belong to space group $P2_1/c$. The unit cell constants given in Table II have been refined by least squares from angular data for 25 reflections.

Diffraction data were collected on an Enraf-Nonius CAD 4 automated diffractometer at −100 °C. A variation of 10% in the intensities of the standard reflections recorded periodically was observed during the data collection. Intensities were corrected for Lorentz and polarization factors but not for absorption. All computations were performed on a PDP 11/44 computer; the structure was solved by direct methods (Multan)[5] and refined with the SDP software[6] by a combination of Patterson, difference-Fourier, and full-matrix least-squares refinement techniques using anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were placed in calculated positions with isotropic temperature factors fixed at 5 Å^2 and were not refined; these values were included in the final full-matrix refinement of all non-hydrogen atoms. The function minimized was $\sum w(|F_o| - F_c|)^2$, where $w = V_o/\sigma^2$. Final R and R_w values were respectively 0.049 and 0.051. The atomic scattering factors were taken from ref 24.

Results

The transformations observed in this study are summarized in Scheme I.

(1) Nitrosyl HMPA Complexes. Allowing $[Fe(NO)_2(Cl)]_2$ (**1**) and HMPA (P═O:Fe = 1:1) to react under an argon atmosphere yielded a most unstable species, **2**, which we could not fully characterize. However, the IR data (KBr pellets) for **2** show two ν(NO) vibrations at 1699 and 1761 cm^{-1}, coordinated ν(P═O) at 1192 cm^{-1} (ν(P═O) for free HMPA 1220 cm^{-1}), and one ν(FeCl) vibration at 324 cm^{-1}, consistent with the $Fe(NO)_2(Cl)(HMPA)$ formulation. Complex **2** is paramagnetic, giving a single line even at very low temperatures ($g = 2.037$). Attempts to get reproducible elemental analysis of the gray product **2** failed, probably due to its tremendous instability even in the solid state. It is noteworthy that, to our knowledge, no stable complex of iron dinitrosyl with a Fe–O–P moiety is noted in the literature.

In solution, **2** reacts with formation of brown fumes: from a dichloromethane–pentane solution of **2** kept at 0 °C, we could separate a green crystalline product that is analyzed as $Fe(NO)(Cl)_2(HMPA)\cdot{}^1/_2HMPA$ (**3**) and is characterized, in the IR spectrum, by a single ν(NO) band at 1776 cm^{-1} and two ν(FeCl) bands at 330 and 376 cm^{-1}. From the brown residue that is left after separation of **3** and accounts for ca. 50% of the starting iron, no pure compound could be isolated in our hands; however, the IR spectrum shows no vibration in the region assigned to the Fe–NO moiety, while vibrations measured at 3375 and 680 cm^{-1}

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(5) Main, P.; Fiske, S. J.; Hall, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. "*Multan 80. A System of Computer Programs for Automatic Solution of Crystal Structures from X-ray Diffraction Data*"; University of York, York, England, and University of Louvain, Louvain, Belgium, 1980.

(6) Frenz, B. A. In *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., Van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, The Netherlands, 1978; pp 44–71.

were taken to indicate the formation of hydrated μ-oxo iron species.[7]

It is noteworthy that this transformation of **2**, characterized by the loss of NO, differs from that observed for $Fe(NO)_2(Cl)(PPh_3)$:[8] in the presence of PPh_3 this latter species loses chlorine to yield $Fe(NO)_2(PPh_3)_2$, where the $Fe(NO)_2$ moiety is maintained.

(2) Fe–NO → Fe–NO_3 Oxidation. Bubbling oxygen into solutions of the dinitrosyl complex **2** or of the mononitrosyl complex **3** in dichloromethane caused a rapid change in color from gray-black (**2**) or green (**3**) to yellow in less than 5 min; it is noteworthy that some brown fumes were observed during the oxygenation of **2**. After treatment of the reaction mixtures, the same yellow compound **4**, which is analyzed as $Fe(NO_3)(Cl)_2(HMPA)\cdot{}^1/_2HMPA$, was obtained from both **2** and **3**. The reaction is quantitative when starting from **3** while, in the case of **2**, ca. 50% of the iron is lost through decomposition into hydrated oxo species. The IR spectra measured for **4** (KBr pellets) showed the complete disappearance of the nitrosyl vibrations, while new absorptions were measured at 1528, 1280, and 808 cm^{-1} in the regions generally assigned to bound nitrates.[9] Furthermore, these frequency bands are at about the same wavenumbers as those for $Fe(TPP)(NO_3)$[10] and $Fe(Salen)(NO_3)$,[11] where the nitrates are known to be bidentate. On the other hand, there was no IR spectral indication for the formation of nitro or nitrito groups, and this was further supported by specific analysis of the NO_3 and NO_2 groups.

When the oxygenation reaction of **2** was conducted in dichloromethane together with an excess of HMPA, the solution was found to be a mixture of both $Fe(NO_3)(Cl)_2(HMPA)_2$ (**7**) and $Fe(NO_3)_2(Cl)(HMPA)_2$ (**8**), as was easily demonstrated through independent preparations of these two complexes from anhydrous iron(III) chloride, HMPA, and silver nitrate in acetonitrile.

By very slow evaporation of this solution in dichloromethane, yellow parallelpiped-shaped crystals were obtained. Their infrared spectrum (KBr pellet) was identical with that of $Fe(NO_3)(Cl)_2(HMPA)_2$ (**8**) prepared by direct methods, and microanalysis confirmed the formulation of the complex. The structure of compound **8** was unambiguously established by a single-crystal X-ray study (vide infra).

On the other hand, direct oxidation of the chlorodinitrosyliron dimer $[Fe(NO)_2(Cl)]_2$ (**1**) by molecular oxygen (1 atm) in the presence of HMPA (P=O:Fe = 1:1) in acetonitrile at room temperature yielded compound **6**, which was isolated (45%) from the oily residue of the reaction mixture and is analyzed as $Fe(NO_3)_2(Cl)(HMPA)\cdot{}^1/_2HMPA$.

The oxidation of the nitrosyl groups in **1** into nitrato—and, once again, not nitro—groups in **6** is evidenced in the IR spectrum (KBr pellets), where the $\nu(NO_3)$ stretching frequencies are measured at 1550, 1524, and 1281 cm^{-1} (Table I). The presence of coordinated HMPA is ascertained by a ν(P=O) vibration at 1188 cm^{-1}; the ν(P=O) vibration expected at 1220 cm^{-1} for free HMPA is not clearly measured due to the broadness of the signals in this region. A vibration band at 380 cm^{-1} is assigned to the FeCl moiety.

When conducted in the presence of 2 equiv of HMPA per iron atom in dichloromethane or acetonitrile at room temperature, the oxygenation of $[Fe(NO)_2(Cl)]_2$ yielded exclusively $Fe(NO_3)_2(Cl)(HMPA)_2$ (**7**). This reaction, which affords a bis(nitrato) complex, compares well with the oxidation of $[Fe(NO)_2(Cl)]_2$ by O_2 in the presence of PPh_3 or $OPPh_3$ (P or P=O:Fe = 2:1), which we have shown to yield the bis(nitrato) complex $Fe(NO_3)_2(Cl)(OPPh_3)_2$.[3] The infrared spectrum for **7** shows $\nu(NO_3)$ at 1510, 1283, and 808 cm^{-1}, a shifted ν(P=O) band at 1190 cm^{-1}, and one ν(FeCl) vibration at 350 cm^{-1}, clearly showing that **7** is different from both **4** and **6**.

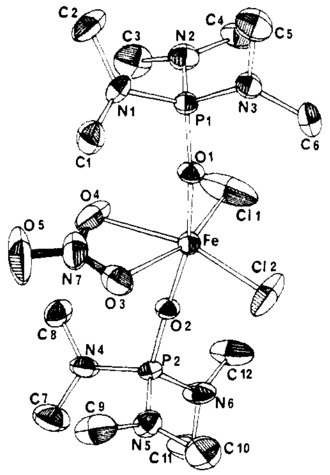

Figure 1. Molecular structure of $Fe(NO_3)(Cl)_2(HMPA)_2$ (**8**). Hydrogen atoms are omitted for clarity. Vibrational ellipsoids are drawn at the 50% probability level.

Table III. Selected Bond Distances (Å) and Angles (deg) with Esd's for **8**

Fe–Cl_1	2.257 (1)	O_1–P_1	1.507 (2)
Fe–Cl_2	2.273 (1)	O_2–P_2	1.506 (2)
Fe–O_1	1.966 (2)	P_1–N_1	1.643 (3)
Fe–O_2	1.963 (2)	P_1–N_2	1.639 (3)
Fe–O_3	2.165 (3)	P_1–N_3	1.637 (3)
Fe–O_4	2.226 (3)	P_2–N_4	1.630 (3)
O_3–N_7	1.263 (5)	P_2–N_5	1.638 (3)
O_4–N_7	1.273 (6)	P_2–N_6	1.634 (3)
O_5–N_7	1.232 (5)		
O_3–Fe–O_4	58.6 (1)	O_1–Fe–O_2	166.8 (1)
O_3–N_7–O_4	116.0 (4)	Cl_1–Fe–Cl_2	106.94 (7)
O_5–N_7–O_4	121.8 (6)	Fe–O_1–P_1	154.2 (2)
O_5–N_7–O_4	122.1 (6)	Fe–O_2–P_2	154.2 (2)

(3) X-ray Crystal Structure of $Fe(NO_3)(Cl)_2(HMPA)_2$ (8). The structure of the compound $Fe(NO_3)(Cl)_2(HMPA)_2$ (**8**) is illustrated in Figure 1 with the atom labeling used. Selected bond lengths and angles together with estimated standard deviations are given in Table III.

The geometry of the complex is that of a distorted octahedron with the two HMPA ligands at the apices and the two chlorine atoms and two oxygen atoms of the nitrate ligand forming a square-planar arrangement around the iron atom. The two bulky HMPA ligands are trans to each other, which minimizes steric interactions.

The nitrate ligand, the two chlorine atoms, and the iron atom are planar within 0.01 Å. The dihedral angles between FeO_1P_1 and FeO_2P_2 planes with the $FeNO_3$ plane are 83.6 and 96.5° respectively, and the dihedral angle between the two FeOP planes is 21.3°.

The iron–nitrate structural parameters are very similar to those found for other symmetrical bidentate nitrato complexes.[12] The difference between the distances of the iron atom and the two coordinated oxygen atoms of the nitrato group is 0.061 Å, i.e. on the order of magnitude where the nitrate ligand is considered to be symmetrically bidentate.[12] As for the bond lengths, Fe–O_3 and Fe–O_4 were found to be much longer than the sum of Shannon's ionic radii[13] (Fe–O = 2.00 Å), and the bond is thought to be weak.

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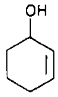
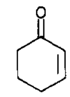
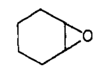
Table IV. Oxidation of Cyclohexene in the Presence of Iron Nitrate HMPA Complexes at Room Temperature after 72 h[a]

complex	solvent	yield of products,[b] %[c]			turnover[d]
					
$Fe(NO_3)(Cl_2)(HMPA)\cdot{}^1/_2HMPA$ (**4**)	CH_2Cl_2	58	42	traces	10
	CH_3CN	55	45	traces	25
$Fe(NO_3)_2(Cl)(HMPA)\cdot{}^1/_2HMPA$ (**6**)	CH_2Cl_2	80	20		7
	CH_3CN	56	44		24
$Fe(NO_3)_2(Cl)(HMPA)_2$ (**7**)	CH_2Cl_2	54	46	traces	14
	CH_3CN	54	46	traces	15
$Fe(NO_3)(Cl)_2(HMPA)_2$ (**8**)	CH_2Cl_2	0	0	0	0
	CH_3CN	70	30	traces	8

[a] Conditions: O_2 (1 atm); concentration of complex 2×10^{-2} M^-; [cyclohexene]/[complex] = 100. [b] Identified by GS–MS coupling. [c] GC determination using octane as internal standard; yields based on iron. [d] Turnover = moles of products/moles of complex.

The O_3–N_7–O_4 angle involving both coordinated oxygens is less than 120° (116.0°). The terminal N_7–O_5 bond (1.232 (5) Å) is slightly shorter than the N–O bonds involving coordinated oxygens (1.263 (5) and 1.273 (6) Å). Diffraction data were collected at −100 °C owing to the high value of the isotropic thermal parameter of the oxygen atom O_5 (ca. 20 Å^2) observed at room temperature. Nevertheless, the value is still relatively large (11.9 Å^2).

The Fe–Cl distances (2.257 (1) and 2.273 (1) Å) are comparable to that found for $Fe(NO_3)_2(Cl)(OPPh_3)_2$[3] (2.257 (1) Å) within experimental uncertainties. The HMPA groups have the usual geometry[14,15] with a nonlinear Fe–O–P moiety (154.2 (2)°) and P–O bond lengths of 1.506 (2) and 1.507 (2) Å. The average of the six P–N bond lengths is 1.637 (7) Å, and the average sum of the angles (356°) around the nitrogen atoms indicates that they have an essentially planar configuration.

(4) Reactivities. The HMPA nitrato complexes **4**, **6**, **7**, and **8** were all found to be most reluctant to react with olefins under anaerobic conditions. No reaction was observed between **4**, **6**, **7**, or **8** and cyclohexene (in a 10:1 olefin:Fe ratio) after 72 h at room temperature under argon: the unaltered nitrato complexes were quantitatively recovered.

On the other hand, the pentacoordinated mononitrate **8** and dinitrate **7** were found to react rapidly with phosphines even in the absence of oxygen.

Thus, IR monitoring of the reaction between **7** and PPh_3 (10-fold excess) under argon, in CH_2Cl_2 or CH_3CN, shows the rapid disappearance of the $\nu(NO_3)$ vibrations in **7** while $OPPh_3$ and coordinated NO groups become detectable. Treatment of the reaction mixture afforded on the one hand (i) free $OPPh_3$ (2–4 equiv) and HMPA, easily separated through washing with ethanol, and (ii) the iron residue, which, as clearly evidenced by IR data, is a mixture of $Fe(NO)_2(PPh_3)_2$ and $Fe(NO)_2(Cl)(PPh_3)$. The formation of these last two nitrosyl adducts can be accounted for by (i) oxygen transfer from **7** to PPh_3 to yield $OPPh_3$ and $Fe(NO)_2(Cl)(HMPA)_2$ as the reduced form of **7** followed by (ii) substitution of HMPA by PPh_3 in the coordination sphere of iron, due to both concentration and coordination ability effects, to form $Fe(NO)_2(Cl)(PPh_3)_2$, for which transformation into $Fe(NO)_2(PPh_3)_2$ and $Fe(NO)_2(Cl)(PPh_3)$ has already been reported.[3,8]

In the reaction of the mono(nitrato) complex **8** with PPh_3 (10-fold excess) a change of color from yellow to green occurred; the iron residue shows a single $\nu(NO)$ vibration at 1800 cm^{-1} in the IR spectrum but could not be isolated in our hands owing to its extreme sensitivity.

On the other hand, **4** and **6** were found not to transfer oxygen even to PPh_3.

The nitrate complexes **4**, **6**, **7**, and **8** are nevertheless catalysts in the oxidation of cyclohexene by molecular oxygen. They catalyze the aerobic oxidation of cyclohexene to cyclohex-1-en-3-one and cyclohex-1-en-3-ol, cyclohexene oxide being formed only in trace amounts (Table IV). The products of the reaction mixture were identified by GLC–MS coupling after 72 h and comparison of their mass spectra with those of authentic samples.

The formation of cyclohex-1-en-3-one and cyclohex-1-en-3-ol, which are typical autoxidation products of cyclohexene, suggests that the iron species are simply decomposing the reaction intermediate, cyclohexenyl hydroperoxide, as found for other iron complexes and for various group VIII metal complexes.[16–18] Indeed, the oxidation of cyclohexene in the presence of the iron complexes was found to be severely inhibited when a radical trap, 2,6-di-*tert*-butyl-4-methylphenol, was added to the reaction mixture.

During the course of the reaction a brown precipitate was formed, indicating decomposition of the iron complex. Nevertheless, there seemed to be no effect on the rate of autoxidation of cyclohexene, confirming further that the oxidation of cyclohexene in the presence of these iron complexes is most probably radical-initiated.

The yields and distribution of the reaction products depend upon the nature of the iron catalyst and the solvent: acetonitrile gives higher activities than dichloromethane. However, the results in Table IV seem difficult to rationalize: the $Fe(NO_3)(Cl)_2$ moiety seems to induce higher reactivities, but no selectivity, when comparing **7** and **8**, which are both pentacoordinated, but the opposite effect is found for **6** as compared to that for **4**.

Discussion

Oxygenation of coordinated nitric oxide by molecular oxygen generally results in the formation of nitro compounds. Our results add to the few examples in the literature where cobalt,[19] iridium,[20] platinum,[21] ruthenium,[22] or iron[3] nitrosyl complexes react with oxygen to form nitrato species.

Oxidation of the Fe–NO moiety by molecular oxygen in the presence of HMPA affords exclusively nitrato—and not nitro—complexes, as was the case in the presence of PPh_3 or $OPPh_3$.[3] However, the HMPA ligand induces reactivities that are in marked contrast with those observed with PPh_3: the loss of NO in **2** produces the mononitrates **4** and **6**. Furthermore, the HMPA ligand, probably owing to its size, obviously favors the stoichiometry observed in **3**, **4**, and **6**: similarly, anhydrous iron(III) chloride, when reacted with HMPA even in excess (up to 4 equiv) yields systematically $Fe(Cl)_3(HMPA)\cdot{}^1/_2HMPA$ (**5**) instead of $Fe(Cl)_3(HMPA)_2$ or $[Fe(Cl)_4][Fe(Cl)_2(HMPA)_4]$, which we expected through analogy with the adducts that form when $Fe(Cl)_3$ is allowed to react with $OPPh_3$.[23]

The nitrato ligands in the pentacoordinated nitrates $Fe(NO_3)_2(Cl)(HMPA)_2$ (**7**) and $Fe(NO_3)(Cl)_2(HMPA)_2$ (**8**) are capable of transferring oxygen to phosphines, and this oxygen transfer regenerates the nitrosyl moiety.

It is noteworthy that $Fe(NO_3)(Cl)_2(HMPA)\cdot{}^1/_2HMPA$ (**4**) and $Fe(NO_3)_2(Cl)(HMPA)\cdot{}^1/_2HMPA$ (**6**) have lost all oxygen-transfer properties. In compounds **4** and **6**, when compared with **7** and **8**, (i) the coordination sphere of the iron atom is less crowded, which should favor the coordination of the substrate, and (ii) the electron density on the metal, and therefore on the nitrato group, is lower. A key factor for an oxidizing Fe–NO/Fe–NO_3 cycle thus appears to be enhanced electron density on the nitrato group.

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We take these results to further support our hypothesis that the Fe–NO/Fe–NO_3 redox couple inherently constitutes an alternative for the O_2 oxidation of organic substrates if the appropriate ligand environment can be designed. The Fe–NO_3 → Fe–NO transformation, i.e. the oxygen-transfer step, is obviously the most demanding.

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Supplementary Material Available: Tables containing crystallographic data for $Fe(NO_3)(Cl)_2(HMPA)_2$, positional parameters, thermal parameters, bond distances and angles, and torsional angles and least-squares planes and a figure illustrating the unit cell packing arrangement (12 pages); a table of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of Paramagnetic Trinickel–Molybdenum and Trinickel–Tungsten Clusters

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Thermolysis of the heterodinuclear complexes $NiM(CO)_4(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)$ (M = Mo, W) leads to the formation of the tetranuclear paramagnetic complexes $Ni_3M(\mu_3\text{-}CO)_3(\eta^5\text{-}C_5H_5)_3(\eta^5\text{-}C_5H_4Me)$ (M = Mo, **1a**; M = W, **1b**) that exhibit a spin equilibrium. The structure of **1a** has been determined by a low-temperature X-ray diffraction study. **1a** crystallizes in the orthorhombic space group $P2_12_12_1$ (No. 19) with $a = 14.522$ (5) Å, $b = 9.587$ (2) Å, $c = 15.128$ (4) Å, and $Z = 4$ at −155 °C. The structure was solved and refined by using 1847 reflections with $F > 2.33\sigma(F)$. **1a** consists of an approximately isosceles nickel atom triangle capped by a methylcyclopentadienyl–molybdenum unit. All the nickel–nickel bonds are long, one being significantly longer than the other two. The three molybdenum–nickel bond lengths are normal and equal within statistical error. Each dinickel–molybdenum face is capped by a triply semibridging carbonyl ligand. Magnetic measurements of solutions of **1a** at various temperatures reveal that the unpaired electron density in the cluster varies with temperature, suggesting the possibility of a spin equilibrium. Complex **1b** exhibits similar behavior. Solutions or powder samples of **1a** and **1b** afford no observable ESR signals at ambient temperatures. The clusters **1a**, **1b**, $Ni_3Mo(\mu_3\text{-}CO)_3(\eta^5\text{-}C_5H_5)_4$ (**1c**), and $Ni_3Mo(\mu_3\text{-}CO)_3(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)_3$ (**2**) may be prepared by alternative synthetic routes. **1c** and **2** also exhibit anomalous chemical shifts in their ^1H NMR spectra and appear to be paramagnetic at ambient temperatures. Mechanistic insights into the formation of these clusters are presented.

Introduction

Paramagnetic organometallic clusters with the metals in low formal oxidation states are relatively unusual species, and limited examples are recognized. Among them are the cluster complex $Ni_3(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_5)_3$[2a] and its analogues, extensively studied by Dahl and co-workers.[2b,c] Other examples include the tricobalt clusters $Co_3(\eta^5\text{-}C_5H_4R)_3(\mu_3\text{-}S)_2$ (R = H, Me),[3] $Co_3(CO)_9X$ (X = S, Se),[4] and $Co_3(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5Me_5)_3$,[5] the cobalt–iridium species $Co_2Ir(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5Me_5)$,[6] and the nickel clusters $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}S)_2$[7] and $Ni_4(\mu\text{-}H)_3(\eta^5\text{-}C_5H_5)_4$.[8] A series of trinuclear clusters of general formula $[(\eta^5\text{-}C_5Me_5)\text{-}M]_{3-n}[(\eta^5\text{-}C_5H_5)Co]_n(\mu_3\text{-}CO)_2$ (M = Co, Rh; n = 1, 2), analogous to $Co_3(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5Me_5)_3$, has recently been reported.[9]

Table I. Crystallographic Data for $Ni_3Mo(\mu_3\text{-}CO)_3(\eta^5\text{-}C_5H_5)_3(\eta^5\text{-}C_5H_4Me)$ (**1a**)

chem formula	$C_{24}H_{22}MoNi_3O_3$	fw	630.51
a^a	14.522 (5) Å	space group	$P2_12_12_1$ (No. 19)
b^a	9.587 (2) Å	T	−155 °C
c^a	15.128 (4) Å	λ	0.71069 Å
V	2106.16 $Å^3$	d_{calcd}	1.988 g cm^{-3}
Z	4	μ	32.505 cm^{-1}
R^b	4.26%	R_w	4.17%

[a] 40 reflections. [b] $R\ \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = 1/\sigma^2(|F_o|)$.

We have been investigating reactions of the mixed-metal complexes $NiM(CO)_4(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)$ (M = Mo, W) with various reagents.[10] In an attempt to synthesize heterodimetallic olefin complexes, we serendipitously prepared new tetranuclear paramagnetic trinickel–molybdenum and trinickel–tungsten cluster species whose temperature-dependent ^1H NMR behavior is reminiscent of that exhibited by paramagnetic tricobalt complexes.[3,5,9]

Results and Discussion

Synthesis and Characterization. Treatment of the heterodimetallic complex $(\eta^5\text{-}C_5H_5)(CO)Ni\text{–}Mo(CO)_3(\eta^5\text{-}C_5H_4Me)$ with hot 1,5-cyclooctadiene yielded a red-brown solution over a 3-h

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