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 $[(\eta^5\text{-}C_5Me_5)M]_{3-n}[(\eta^5\text{-}C_5H_5)Co]_n(\mu_3\text{-}CO)_2$ (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]

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]

**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 | $\mu$ | 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 $w = 1/\sigma^2(|F_o|)$.

## 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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**Table II.** Fractional Coordinates ($\times 10^4$) for **1a** with Esd's in Parentheses

| atom | *x* | *y* | *z* | atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Mo(1) | 2415 (1) | −98 (1) | 8886 (1) | Ni(2) | 3271 (1) | 1990 (2) | 8168 (1) |
| Ni(3) | 1558 (1) | 2019 (2) | 8201 (1) | Ni(4) | 2364 (1) | 2313 (1) | 6965 (1) |
| C(5) | 2410 (9) | 449 (10) | 7588 (7) | O(5) | 2400 (6) | 195 (8) | 6834 (5) |
| C(7) | 1326 (8) | 893 (14) | 9450 (9) | O(8) | 611 (5) | 837 (10) | 9805 (7) |
| C(9) | 3497 (8) | 875 (16) | 9406 (9) | O(10) | 4211 (5) | 921 (10) | 9797 (7) |
| C(11) | 2419 (10) | −1949 (11) | 9852 (7) | C(12) | 1622 (9) | −2033 (17) | 9344 (12) |
| C(13) | 1873 (10) | −2271 (17) | 8481 (10) | C(14) | 2859 (9) | −2318 (14) | 8438 (8) |
| C(15) | 3201 (9) | −2194 (17) | 9314 (10) | C(16) | 4167 (9) | −2262 (15) | 9611 (11) |
| C(17) | 4669 (9) | 1985 (18) | 7787 (10) | C(18) | 4527 (8) | 3185 (17) | 8308 (11) |
| C(19) | 3833 (10) | 3991 (17) | 7889 (12) | C(20) | 3633 (10) | 3328 (21) | 7072 (11) |
| C(21) | 4126 (10) | 2112 (18) | 7047 (10) | C(22) | 131 (9) | 2092 (18) | 7933 (10) |
| C(23) | 373 (9) | 3318 (17) | 8368 (10) | C(24) | 1024 (9) | 4022 (16) | 7820 (12) |
| C(25) | 1164 (9) | 3210 (16) | 7043 (10) | C(26) | 612 (8) | 2008 (18) | 7124 (9) |
| C(27) | 2908 (8) | 2837 (14) | 917 (8) | C(28) | 3185 (9) | 3879 (17) | 331 (11) |
| C(29) | 2383 (11) | 4479 (12) | 9957 (9) | C(30) | 1606 (10) | 3890 (16) | 360 (11) |
| C(31) | 1916 (8) | 2860 (19) | 958 (8) | | | | |

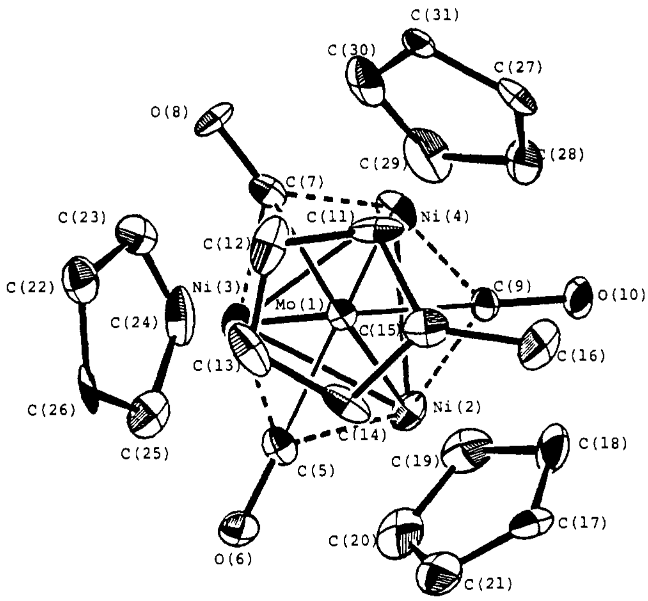


**Figure 1.** Labeled ORTEP plot of $Ni_3Mo(\mu_3\text{-}CO)_3(\eta^5\text{-}C_5H_5)_3(\eta^5\text{-}C_5H_4Me)$ (**1a**), showing the thermal ellipsoids at the 50% probability level. The view shown is approximately perpendicular to the trinickel plane. Hydrogen atoms and metal–cyclopentadienyl bonds are omitted for clarity.

period. Chromatography on silica gel or alumina resulted in substantial decomposition; the only product recovered was the dimolybdenum complex $[Mo(CO)_3(\eta^5\text{-}C_5H_4Me)]_2$. However, in addition to this species, a brownish black product was eluted off a Florisil column; the solution yielded black crystals when concentrated and placed in a −20 °C freezer.

The $^1H$ NMR spectra of solutions of this species (**1a**) exhibited an AA′BB′ multiplet and a singlet for the proton signals of a methylcyclopentadienyl group; in addition, an unusual resonance, integrating for 15 hydrogen atoms, was observed at $\delta = -3.39$ ppm at 20 °C. This chemical shift was highly temperature dependent, shifting downfield with decreasing temperature ($\delta = +3.53$ ppm at −100 °C) and upfield with increasing temperatures ($\delta = -10.68$ ppm at 90 °C). Slight broadening of this signal also occurred at higher temperatures; in contrast, chemical shifts of the aromatic and aliphatic methylcyclopentadienyl protons were essentially temperature invariant.

The IR spectrum of dichloromethane solutions of **1a** exhibited a strong band at 1718 $cm^{-1}$, in the absorption range of triply bridging carbonyl ligands. The mass spectrum exhibited a parent peak with an isotopic envelope characteristic of a trinickel–molybdenum species. **1a** was proposed to be the heteronuclear cluster species $Ni_3Mo(\mu_3\text{-}CO)_3(\eta^5\text{-}C_5H_5)_3(\eta^5\text{-}C_5H_4Me)$ on the basis of $^1H$ NMR, IR, and MS data: a low-temperature X-ray diffraction study carried out on a single crystal of **1a** confirmed this proposed structure. An ORTEP plot perpendicular to the trinickel plane is shown in Figure 1, while a side view of the molecule is shown in

**Table III.** Key Bond Distances (Å) for **1a** with Esd's in Parentheses

| | | | |
|---|---|---|---|
| Mo(1)–Ni(2) | 2.594 (2) | Mo(1)–Ni(3) | 2.597 (2) |
| Mo(1)–Ni(4) | 2.590 (2) | Ni(2)–Ni(3) | 2.489 (2) |
| Ni(2)–Ni(4) | 2.627 (2) | Ni(3)–Ni(4) | 2.510 (2) |
| Mo(1)–C(5) | 2.032 (11) | Mo(1)–C(7) | 2.033 (13) |
| Mo(1)–C(9) | 1.989 (12) | Ni(2)–C(5) | 2.125 (11) |
| Ni(2)–C(9) | 2.181 (15) | Ni(3)–C(5) | 2.157 (11) |
| Ni(3)–C(7) | 2.202 (13) | Ni(4)–C(7) | 2.055 (13) |
| Ni(4)–C(9) | 2.179 (14) | O(6)–C(5) | 1.167 (13) |
| O(8)–C(7) | 1.170 (14) | O(10)–C(9) | 1.194 (15) |
| Mo(1)–C(CO) | 2.02 (mean) | Ni–C(CO) | 2.15 (mean) |
| Mo(1)–C(Cp′) | 2.33 (mean) | Ni–C(Cp) | 2.14 (mean) |
| C(Cp′)–C(Cp′) | 1.41 (mean) | C(Cp)–C(Cp) | 1.41 (mean) |

**Table IV.** Key Bond Angles (deg) for **1a** with Esd's in Parentheses

| | | | |
|---|---|---|---|
| Ni(2)–Mo(1)–Ni(3) | 57.30 (5) | Ni(2)–Mo(1)–Ni(4) | 60.90 (6) |
| Ni(3)–Mo(1)–Ni(4) | 57.89 (6) | Mo(1)–Ni(2)–Ni(3) | 61.41 (7) |
| Mo(1)–Ni(2)–Ni(4) | 59.48 (5) | Mo(1)–Ni(3)–Ni(2) | 61.29 (7) |
| Mo(1)–Ni(3)–Ni(4) | 60.91 (5) | Mo(1)–Ni(4)–Ni(2) | 59.63 (5) |
| Mo(1)–Ni(4)–Ni(3) | 61.20 (6) | Ni(3)–Ni(2)–Ni(4) | 58.70 (7) |
| Ni(2)–Ni(4)–Ni(3) | 57.90 (6) | Ni(2)–Ni(3)–Ni(4) | 63.40 (7) |
| Ni(2)–Mo(1)–C(5) | 53.0 (3) | Ni(2)–Mo(1)–C(7) | 100.8 (4) |
| Ni(2)–Mo(1)–C(9) | 54.9 (4) | Ni(3)–Mo(1)–C(5) | 53.9 (3) |
| Ni(3)–Mo(1)–C(7) | 55.2 (4) | Ni(3)–Mo(1)–C(9) | 99.8 (4) |
| Ni(4)–Mo(1)–C(5) | 101.8 (3) | Ni(4)–Mo(1)–C(7) | 51.1 (4) |
| Ni(4)–Mo(1)–C(9) | 55.0 (4) | C(5)–Mo(1)–C(7) | 106.4 (5) |
| C(5)–Mo(1)–C(9) | 105.3 (5) | C(7)–Mo(1)–C(9) | 103.3 (4) |
| Mo(1)–Ni(2)–C(5) | 49.8 (3) | Mo(1)–Ni(2)–C(9) | 48.3 (3) |
| Mo(1)–Ni(3)–C(5) | 49.6 (3) | Mo(1)–Ni(3)–C(7) | 49.3 (3) |
| Mo(1)–Ni(4)–C(7) | 50.3 (4) | Mo(1)–Ni(4)–C(9) | 48.4 (3) |
| Mo(1)–C(5)–Ni(2) | 77.2 (4) | Mo(1)–C(5)–Ni(3) | 76.5 (4) |
| Mo(1)–C(7)–Ni(3) | 75.5 (4) | Mo(1)–C(7)–Ni(4) | 78.6 (4) |
| Mo(1)–C(9)–Ni(2) | 76.8 (5) | Mo(1)–C(9)–Ni(4) | 76.7 (4) |
| Mo(1)–C(5)–O(6) | 153.0 (8) | Mo(1)–C(7)–O(8) | 149.5 (11) |
| Mo(1)–C(9)–C(10) | 154.0 (12) | Ni(2)–C(5)–Ni(3) | 71.1 (3) |
| Ni(3)–C(7)–Ni(4) | 72.2 (4) | Ni(2)–C(9)–Ni(4) | 74.1 (5) |
| Ni(3)–Ni(2)–C(5) | 55.1 (3) | Ni(3)–Ni(2)–C(9) | 98.0 (3) |
| Ni(4)–Ni(2)–C(5) | 98.1 (3) | Ni(4)–Ni(2)–C(9) | 52.9 (4) |
| Ni(2)–Ni(3)–C(5) | 53.9 (3) | Ni(2)–Ni(3)–C(7) | 99.5 (3) |
| Ni(4)–Ni(3)–C(5) | 100.8 (3) | Ni(4)–Ni(3)–C(7) | 51.2 (3) |
| Ni(2)–Ni(4)–C(7) | 99.2 (4) | Ni(2)–Ni(4)–C(9) | 53.0 (4) |
| Ni(3)–Ni(4)–C(7) | 56.6 (4) | Ni(3)–Ni(4)–C(9) | 97.4 (4) |
| Ni(2)–C(5)–O(6) | 123.8 (9) | Ni(3)–C(5)–O(6) | 124.0 (9) |
| Ni(3)–C(7)–O(8) | 123.6 (10) | Ni(4)–C(7)–O(8) | 127.7 (11) |
| Ni(2)–C(9)–O(10) | 122.5 (10) | Ni(4)–C(9)–O(10) | 123.1 (11) |
| C(5)–Ni(2)–C(9) | 95.9 (5) | C(5)–Ni(3)–C(7) | 96.6 (4) |
| C(7)–Ni(4)–C(9) | 96.2 (4) | | |

Figure 2. Selected data collection parameters are listed in Table I; Tables II–IV list fractional atomic coordinates with isotropic thermal parameters and key bond lengths and bond angles, respectively.

**Structural Features of $Ni_3Mo(\mu_3\text{-}CO)_3(\eta^5\text{-}C_5H_5)_3(\eta^5\text{-}C_5H_4Me)$ (1a).** The metallic core of **1a** consists of a distorted tetrahedron of three nickel atoms and a molybdenum atom. Each metal is bound to a $\eta^5\text{-}C_5H_4Me$ ligand (molybdenum) or a $\eta^5\text{-}C_5H_5$ ligand (nickel). The three nickel–molybdenum distances are unre-

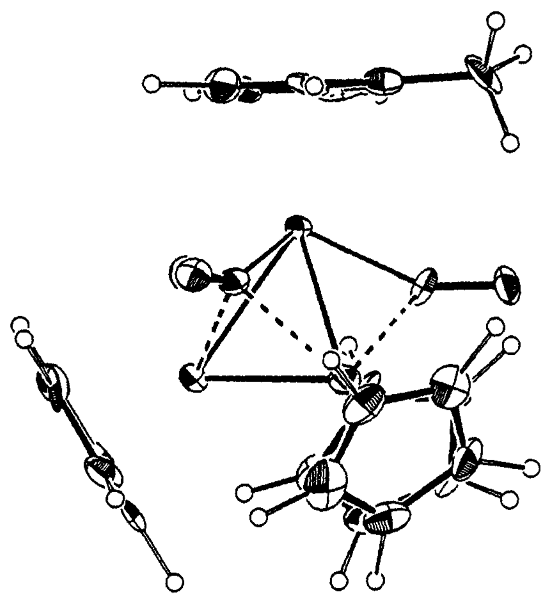

**Figure 2.** ORTEP plot of **1a**, showing a view parallel to the trinickel plane (50% probability ellipsoids). A nickel atom and a carbonyl ligand are eclipsed.

markable and not statistically different from each other [Ni–Mo(mean) = 2.593 Å]. Other literature values for nickel–molybdenum bonds are 2.5859 (2) Å for the species $NiMo(CO)_2\{\mu\text{-}\eta^2,\eta^2\text{-}C(Me)C(Me)C(O)\}(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)$,[10] 2.557 (4) and 2.622 (1) Å for the two related complexes $MoNi_2(\mu_3\text{-}CPh)(CO)_2(\eta^5\text{-}C_5H_5)_2$ and $CoNiMo(\mu_3\text{-}CMe)(CO)_5(\eta^5\text{-}C_5H_5)_2$,[11] and 2.616 (2) Å for the alkyne-bridged cluster $FeMoNi(CO)_5(\mu\text{-}PhC_2{}^iPr)(\eta^5\text{-}C_5H_5)_2$.[12] Mean values of 3.064 and 3.151 Å are observed[13] for the pentanuclear anionic cluster $[Mo_2Ni_3(CO)_{16}]^{2-}$, but these long nickel–molybdenum bonds reflect their electron deficiency.

The triangle formed by the three nickel atoms is asymmetric and close to isosceles; two of the nickel–nickel bond lengths are comparable, and the third nickel–nickel distance is significantly longer [Ni(2)–Ni(3) = 2.489 (2) Å; Ni(3)–Ni(4) = 2.510 (2) Å; Ni(2)–Ni(4) = 2.627 (2) Å]. Even the shorter nickel–nickel bonds are longer than values frequently observed in clusters, suggesting a bond order of less than 1 for these bonds. Nickel–nickel bond lengths averaging 2.34 Å are found in the pentanuclear trigonal-bipyramidal cluster anions $[Ni_3M_2(CO)_{16}]^{2-}$ (M = Mo, W).[13] Other nickel–nickel bond lengths observed in clusters are 2.389 (2) Å in the 49-electron cluster $Ni_3(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_5)_3$,[2b] 2.530 (3) Å in the pentamethylcyclopentadienyl analogue $Ni_3(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5Me_5)_3$,[2c] a mean value of 2.421 Å for the three distinct Ni–Ni bond lengths in the monoanion $[Ni_3(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_5)_3]^-$, which contains two unpaired electrons, 2.388 (2) Å for the paramagnetic cluster anion $[CoNi_2(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)_2]^-$,[2c] 2.326 (2) Å for the corresponding diamagnetic cluster $[CoNi_2(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)_2]$,[2b] and 2.373 (1) Å for the cluster $MoNi_2(\mu_3\text{-}CPh)(CO)_2(\eta^5\text{-}C_5H_5)_2$.[11] An average value of 2.46 Å is found for the nickel–nickel bonds in the tetranuclear paramagnetic cluster $Ni_4(\mu_3\text{-}H)_3(\eta^5\text{-}C_5H_5)_4$.[8a]

Molybdenum–cyclopentadienyl carbon bonds are normal, averaging 2.33 Å. Observed nickel–cyclopentadienyl carbon bond lengths in the cluster range from 2.11 to 2.17 Å (mean value 2.14 Å), marginally larger than those commonly observed in diamagnetic complexes but less than values seen in paramagnetic nickel cluster species.[2c] The Ni–C($\mu_3$-CO) bonds have a mean value of 2.15 Å.

The structure may be regarded as consisting of a $Mo(CO)_3(\eta^5\text{-}C_5H_4Me)$ unit interacting with a $[Ni(\eta^5\text{-}C_5H_5)]_3$ triangle. The first example of a species containing a $Mo(CO)_3(\eta^5\text{-}C_5H_5)$ group bonded to three metals, the complex $[Pd(8\text{-methylquinoline})]_3\{\mu_3\text{-}Mo(CO)_3(\eta^5\text{-}C_5H_5)\}(\mu_3\text{-}Cl)BF_4$ was reported by Braunstein and co-workers.[14] There are similar structural features between **1a** and this complex despite the lack of palladium–palladium bonds in the latter species. In both cases, the $M_2Mo$ faces are capped by triply semibridging carbonyl ligands. The Mo–C($\mu_3$-CO) bond lengths and Mo–C–O angles in **1a** are comparable to those found in the molybdenum–tripalladium cluster (mean values are 152° and 2.02 Å for **1a**, compared to 158° and 2.015 Å for Braunstein's cluster). Significant flattening of the $Mo(CO)_3$ tripod is observed in both species: C($\mu_3$-CO)–Mo–C($\mu_3$-CO) angles average 105.0° in **1a** and 106.3° in the molybdenum–tripalladium cluster. In contrast, mean values of 88.1 and 88.3° are found for corresponding angles in the anionic parts of the salts $[NBu_4][Mo(CO)_3(\eta^5\text{-}C_5H_5)]$ and $\{[Mo(CO)_2(PMe)(\eta\text{-}C_5H_5)]_2AsMe_2\}[Mo(CO)_3(\eta^5\text{-}C_5H_5)]$.[15,16]

**Discussion of $^1$H NMR Behavior.** The solid-state structure observed for this cluster is not in accord with the symmetry exhibited in solution, where the cluster is believed to have $C_{3v}$ symmetry on the $^1$H NMR time scale. The large $^1$H NMR chemical shift dependence on temperature observed for this complex mirrors contact shifts observed in paramagnetic molecules and indicates the presence of unpaired electron density in the cluster. Only the chemical shift of the nickel-bound cyclopentadienyl $^1$H NMR resonances varies significantly with temperature, suggesting that unpaired electron density resides in an orbital localized on the three nickel atoms. These chemical shifts should be relatively unaffected by the nature of the capping metal atom. To test this hypothesis, we synthesized the trinickel–tungsten cluster species $Ni_3W(\mu_3\text{-}CO)_3(\eta^5\text{-}C_5H_5)_3(\eta^5\text{-}C_5H_4Me)$ (**1b**), which contains a methylcyclopentadienyl ligand on the tungsten atom. The $^1$H NMR spectrum of this cluster also exhibits a resonance upfield of TMS, whose chemical shift is highly temperature dependent; other $^1$H NMR resonances of **1b** were unaffected by changes in temperature, paralleling the behavior of **1a**. The variation of the cyclopentadienyl $^1$H NMR chemical shift ($\delta$, in ppm) with temperature (°C) for complexes **1a** and **1b** are given respectively by eq 1a and 1b. These equations represent

$$\delta = -0.08060T - 3.460 \qquad (1a)$$

$$\delta = -0.08058T - 4.350 \qquad (1b)$$

empirical least-squares fits to the data (within ±0.05 ppm) in the 20–90 °C temperature range.

**Magnetic Studies.** The magnetic susceptibilities of complexes **1a** and **1b** in solution were determined at various temperatures by using Evans' method.[17] At 40 °C, the magnetic moment of **1a** corresponds to an average value of less than two unpaired electrons per molecule (1.72 $\mu_B$); this value decreases monotonically with temperature over the temperature range studied, dropping to 1.39 $\mu_B$ at -60 °C. The nickel–tungsten cluster **1b** has magnetic moments of 1.19 $\mu_B$ at 20 °C and 0.93 $\mu_B$ at -40 °C. The complexes' low solubility made changes in the solvent density with temperature significant, and corrections for this were necessary.

Despite the paramagnetism of the complexes, toluene solutions or powder samples of **1a** or **1b** do not exhibit ESR signals at ambient temperatures. (A weak signal was detected in some cases. This was attributed, from its *g* value and line shape, to the paramagnetic cluster $Ni_3(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_5)_3$, present as a trace impurity.) ESR and magnetic data are in accord with a temperature-dependent singlet–triplet equilibrium similar to that observed for the tricobalt clusters $Co_3(\eta^5\text{-}C_5H_4R)_3(\mu_3\text{-}S)_2$ (R =

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H, Me)[3] and $Co_3(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5Me_5)_3$.[5] Complex **1a** contains 62 valence electrons, 2 more than the 60 required for an electron-precise tetranuclear closo cluster. The extra electrons reside in an antibonding orbital that appears to be localized on the nickel atoms and not on the molybdenum atom. This is reflected in the longer than average nickel–nickel bonds observed in the X-ray structure of **1a**. Nickel–molybdenum bond lengths in the cluster are normal, in agreement with this argument.

It appears that in the ground state the two antibonding electrons are paired in a nondegenerate orbital. The HOMO–LUMO gap is thermally accessible, resulting in an increase in the fraction of molecules in an electronically excited triplet state with temperature. Such equilibria arise from subtle electronic effects, and small changes in the system may perturb the delicate balance, modifying its magnetic and spectroscopic properties.

We attempted to prepare the cluster complex $Ni_3Mo(\mu_3\text{-}CO)_3(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)_3$ (**2**) to determine whether substitution of the cyclopentadienyl ligands on the nickel atoms with methylcyclopentadienyl ligands substantially modified the physical properties of the cluster. Complex **2** has not yet been obtained free from the trinickel paramagnetic species $Ni_3(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_4Me)_3$, formed as an intermediate in the reaction (and a possible decomposition product of **2**). The solubility properties and behavior of the trinickel cluster and **2** on a Florisil column are almost identical. However, **2** exhibits anomalous temperature-dependent chemical shifts in its $^1$H-NMR spectrum and a singlet–triplet equilibrium appears to be operative here too. Only the (nickel-bound) methylcyclopentadienyl protons appear to be affected by the unpaired electron density in the cluster, and to a lesser extent than for the analogous complex **1a**. Aromatic methylcyclopentadienyl proton chemical shifts resonate upfield of their normal position at $\delta$ = 1.25 and 0.68 ppm, while the methyl resonance is shifted downfield to $\delta$ = 4.30 ppm at 20 °C. At −50 °C, these protons resonate at $\delta$ = 4.13, 3.67, and 2.20 ppm, respectively. Chemical shift differences between methylcyclopentadienyl proton resonances in **2** and those observed in diamagnetic molecules are smaller than differences seen for cyclopentadienyl ligands in **1a** and **1b** and those observed in diamagnetic species. This suggests a larger HOMO–LUMO gap in **2** than in **1a** and **1b**.

**Comments on the Formation of the Clusters.** The clusters are believed to be formed in accordance with eq 2. Cyclooctadiene

$$3NiM(CO)_4(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me) \rightarrow Ni_3M(\mu_3\text{-}CO)_3(\eta^5\text{-}C_5H_5)_3(\eta^5\text{-}C_5H_4Me) + [M(CO)_3(\eta^5\text{-}C_5H_4Me)]_2 + 3CO \quad (2)$$

$$M = Mo, W$$

is not required to synthesize these species and acts only as a solvent; the reaction also proceeds in toluene.

The clusters are also accessible by reacting the species $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ and $[M(CO)_3(\eta^5\text{-}C_5H_4Me)]_2$ (M = Mo, W) in a 3:1 ratio (eq 3). Best yields are obtained by using refluxing

$$3[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2 + [M(CO)_3(\eta^5\text{-}C_5H_4Me)]_2 \rightarrow Ni_3M(\mu_3\text{-}CO)_3(\eta^5\text{-}C_5H_5)_3(\eta^5\text{-}C_5H_4Me) + 6CO \quad (3)$$

$$M = Mo, W$$

tetrahydrofuran (thf) as the solvent, though the reaction proceeds slowly (10–13 days).

We monitored the reaction of $[Mo(CO)_3(\eta^5\text{-}C_5H_4Me)]_2$ with $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ in refluxing thf by FT-IR spectroscopy. Within 2 days, the nickel species $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ was totally consumed. The only carbonyl species present in the IR spectrum of the mixture at this stage appeared to be the initial dimolybdenum complex $[Mo(CO)_3(\eta^5\text{-}C_5H_4Me)]_2$ and the paramagnetic cluster $Ni_3(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_5)_3$. The carbonyl stretch for this cluster, together with those of the molybdenum species, gradually diminished while carbonyl stretches assignable to **1a** grew in.

These data are in accord with a mechanism that involves initial conversion of $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ to the trinickel cluster $Ni_3(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_5)_3$, a reaction known to proceed thermally.[2a] Slow attack on this cluster by a species derived from $[Mo(CO)_3(\eta^5\text{-}C_5H_4Me)]_2$, probably the mononuclear radical species $Mo(CO)_3(\eta^5\text{-}C_5H_4Me)$, follows. This mechanism accounts for the lower yields of **1a** obtained in higher boiling solvents: the complex $[Mo(CO)_3(\eta^5\text{-}C_5H_4Me)]_2$ decarbonylates[18] to form the triply bonded dimeric species $[Mo(CO)_2(\eta^5\text{-}C_5H_4Me)]_2$ when heated. Once formed, this species is unlikely to fragment to mononuclear $Mo(CO)_3(\eta^5\text{-}C_5H_4Me)$ radicals.

To test whether the trinickel cluster was an intermediate, we independently prepared a sample of $Ni_3(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_5)_3$ and reacted it with $[Mo(CO)_3(\eta^5\text{-}C_5H_5)]_2$ in refluxing thf. Carbonyl stretches assignable to the new cluster $Ni_3Mo(\mu_3\text{-}CO)_3(\eta^5\text{-}C_5H_5)_4$ (**1c**), analogous to **1a** and **1b**, appeared in the IR spectrum at 1726 cm$^{-1}$, after 1 week of reflux. This new cluster was fully characterized by $^1$H NMR spectroscopy, MS, and HRMS. Complex **1c**, like the clusters **1a** and **1b**, is also paramagnetic and exhibits a chemical shift upfield of TMS for the nickel-bound cyclopentadienyl resonances at ambient temperatures.

## Conclusions

Paramagnetic 62-electron tetranuclear clusters $Ni_3M(\mu_3\text{-}CO)_3(\eta^5\text{-}C_5H_5)_3(\eta^5\text{-}C_5H_4Me)$ (M = Mo, W) have been prepared by thermolysis of the complexes $NiM(CO)_4(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)$ or by heating the homodinuclear species $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ and $[M(CO)_3(\eta^5\text{-}C_5H_4Me)]_2$ in a 3:1 ratio in thf for 11–13 days. The clusters exhibit a temperature-dependent high-spin–low-spin equilibrium as shown by variable-temperature magnetic studies on **1a** and **1b**. Unpaired electron density is centered on a nickel-localized orbital. The clusters are formed by attack of a $M(CO)_3(\eta^5\text{-}C_5H_4R)$ radical species on the paramagnetic trinickel cluster $Ni_3(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_4R)_3$ (R = H, Me).

Further investigations of the solid-state magnetic behavior of these complexes, their electronic structure, and redox chemistry are in progress.

## Experimental Section

**General Remarks.** All manipulations were carried out under a nitrogen atmosphere by using standard Schlenk or vacuum-line techniques. Solvents were predried over 4-Å molecular sieves. Toluene, 1,5-cyclooctadiene (Aldrich), hexanes, and tetrahydrofuran were distilled over sodium or sodium benzophenone ketyl; dichloromethane was distilled over $CaH_2$. Slight modifications of standard methods were used to prepare $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_4R)]_2$,[19] $[M(CO)_3(\eta^5\text{-}C_5H_4R)]_2$[20] (M = Mo, W; R = H, Me), and $Ni_3(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_5)_3$;[2a] syntheses of $NiM(CO)_4(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)$ (M = Mo, W) have been described previously.[10]

NMR spectra were obtained on a 200-MHz Magnachem A-200 or on a 300-MHz Nicolet NT-300 spectrometer. NMR data were obtained at 20 °C, with $CDCl_3$ as the solvent, unless otherwise stated. An X-band Varian E-9 EPR spectrometer was used to record EPR data. IR spectra were obtained on an IBM IR-32 FT instrument; absorptions are in reciprocal centimeters. Mass spectra were obtained on a Finnegan-Matt 8430 mass spectrometer, PFK was used as the standard for the high-resolution data. All parent peaks showed the expected isotopic envelopes for $Ni_3Mo$ or $Ni_3W$ species. HRMS molecular ion masses are based on $^{58}$Ni and $^{98}$Mo; $^{60}$Ni and $^{183}$W were used for **1b** to minimize isotopomer overlap.

**$Ni_3Mo(\mu_3\text{-}CO)_3(\eta^5\text{-}C_5H_5)_3(\eta^5\text{-}C_5H_4Me)$ (1a). (i) Synthesis from the Heterodinuclear Complex.** $NiMo(CO)_4(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)$ (1300 mg, 3.17 mmol) was dissolved in 1,5-cyclooctadiene (5 mL) and the solution stirred at 70 °C for 3 h. The color of the solution changed from green to reddish brown. 1,5-Cyclooctadiene was removed in vacuo and the residue dissolved in toluene. The solution was filtered through a Celite pad, placed on a Florisil column, and eluted with a hexane/toluene (80:20) mixture, affording the molybdenum complex $[Mo(CO)_3(\eta^5\text{-}C_5H_4Me)]_2$ as a red band. **1a** was eluted as a slowly moving dark brown band with toluene. Recrystallization from toluene afforded **1a** (799 mg, 40%).

**(ii) Synthesis of 1a from Homodinuclear Species.** $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ (911 mg, 3.00 mmol) and $[Mo(CO)_3(\eta^5\text{-}C_5H_4Me)]_2$ (518 mg,

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1.00 mmol) were dissolved in thf (40 mL) and the solution was refluxed in a Schlenk tube under nitrogen; the reaction was monitored periodically by IR spectroscopy. After 2 days, the $\nu$(CO) band of $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ (1847 $cm^{-1}$) had vanished, and a stretch assignable to the cluster $Ni_3(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_5)_3$ appeared at 1752 $cm^{-1}$. IR absorptions assignable to **1a** gradually grew in over an 11-day period as absorptions due to the trinuclear nickel cluster and $[Mo(CO)_3(\eta^5\text{-}C_5H_4Me)]_2$ decreased. The thf was removed in vacuo and the brown-black residue dissolved in toluene. The solution was placed on a Florisil column and eluted with dichloromethane. Subsequent removal of the solvent in vacuo afforded a black powder; recrystallization from toluene yielded the pure product (284 mg, 45%). Spectroscopic data for **1a** as follows. $^1$H NMR: (20 °C) $\delta$ 5.08, 5.01 (m, $[AB]_2$ spin system, 4 H, $C_5H_4Me$), 2.34 (s, 3 H, Me), 3.39 (s, 15 H, $C_5H_5$); (toluene-$d_8$, 90 °C) $\delta$ −10.68 (br s, 15 H, $C_5H_5$); (−100 °C) $\delta$ 3.53 (s, 15 H, $C_5H_5$). Other signals are almost temperature invariant. MS: $m/e$ = 630 ($M^+$), $(M - CO)^+$, $(M - 2CO)^+$, $(M - 3CO)^+$, $(M - CO - 2C_5H_5)^+$. HRMS: calcd for $Ni_3MoC_{24}H_{22}O_3$, $m/e$ 629.868; found, $m/e$ = 629.867. Anal. Calcd for $Ni_3MoC_{24}H_{22}O_3$: C, 45.72; H, 3.52. Found: C, 45.72; H, 4.19. IR [$\nu$(CO)]: (Nujol) 1713 (s) $cm^{-1}$; (dichloromethane) 1718 (s) $cm^{-1}$.

**$Ni_3W(\mu_3\text{-}CO)_3(\eta^5\text{-}C_5H_5)_3(\eta^5\text{-}C_5H_4Me)$ (1b).** The synthesis of **1b** mirrored that of **1a**. A solution of $[Ni(\mu\text{-}CO)(\eta^5\text{-}C_5H_5)]_2$ (911 mg, 3.00 mmol) and $[W(CO)_3(\eta^5\text{-}C_5H_4Me)]_2$ (694 mg, 1.00 mmol) dissolved in thf (40 mL) was refluxed for 13 days. Workup and recrystallization afforded **1b** (690 mg, 48%). Spectroscopic data for **1b** are as follows: $^1$H NMR: $\delta$ 5.20 (s, 4 H, $C_5H_4Me$, resonances are fortuitously coincident), 2.46 (s, 3 H, $C_5H_4Me$), −3.86 (s, 15 H, $C_5H_5$). MS: $m/e$ = 718 ($M^+$), $(M - CO)^+$, $(M - Ni - CO)^+$. HRMS: calcd for $Ni_3WC_{24}H_{22}O_3$, $m/e$ = 721.900; found, 721.906. Anal. Calcd for $Ni_3WC_{24}H_{22}O_3$: C, 40.13; H, 3.09. Found: C, 40.35; H, 3.02. IR [$\nu$(CO)]: (dichloromethane) 1743 (s) $cm^{-1}$.

**Reaction of $Ni_3(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_5)_3$ with $[Mo(CO)_3(\eta^5\text{-}C_5H_5)]_2$ Affording $Ni_3Mo(\mu_3\text{-}CO)_3(\eta^5\text{-}C_5H_5)_4$ (1c).** $Ni_3(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_5)_3$ (214 mg, 0.50 mmol), $[Mo(CO)_3(\eta^5\text{-}C_5H_5)]_2$ (123 mg, 0.25 mmol), and thf (20 mL) were placed in a nitrogen-filled Schlenk tube equipped with a reflux condenser. An initial IR spectrum of the thf solution was taken and showed $\nu$(CO) stretches assignable to the molybdenum dimer [2012 (w), 1956 (s), 1913 (s) $cm^{-1}$] and the trinickel cluster (1752 $cm^{-1}$). After 3 days, bands assignable to $[Mo(CO)_3(\eta^5\text{-}C_5H_5)]_2$ had significantly decreased; $\nu$(CO) stretches of an unknown species were observed at 1863 and 1826 $cm^{-1}$, while the cluster absorption band at 1726 $cm^{-1}$ grew in. After a total of 9 days, the unknown species had been totally consumed and only **1c** and traces of the trinickel species remained. The solvent was removed, the residue was dissolved in dichloromethane, and the solution was filtered through a Celite pad. Recrystallization from dichloromethane afforded pure samples of **1c** (105 mg, 34%). Spectroscopic data for **1c** are as follows. $^1$H NMR: $\delta$ 5.20 (s, 5 H, Mo $C_5H_5$), −4.00 (br s, 15 H, Ni $C_5H_5$). MS: $m/e$ = 658 ($M^+$), $(M - CO)^+$, $(M - 2CO)^+$, $(M - 3CO)^+$, $(M - CO - C_5H_5 - Ni)^+$, $(M - 2CO - C_5H_5 - Ni)^+$, $(M - 3CO - C_5H_5 - Ni)^+$, $(M - 2CO - 2C_5H_5 - Ni)^+$, $(M - 3CO - 2C_5H_5 - Ni)^+$. HRMS: calcd for $Ni_3MoC_{23}H_{20}O_3$, $m/e$ = 615.8527; found, $m/e$ = 615.8490. Anal. Calcd for $Ni_3MoC_{23}H_{20}O_3$: C, 44.81; H, 3.27. Found: C, 44.82; H, 3.34. IR [$\nu$(CO)]: (thf) 1726 (s) $cm^{-1}$.

**$Ni_3Mo(\mu_3\text{-}CO)_3(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Me)_3$ (2).** $[Ni(\mu\text{-}CO)(\eta^5HC_5H_4Me)]_2$ (995 mg, 3.00 mmol) and $[Mo(CO)_3(\eta^5\text{-}C_5H_5)]_2$ (490 mg, 1.00 mmol) were place in a round-bottomed flask equipped with a reflux condenser and a nitrogen adaptor. The system was purged with nitrogen, thf (30 mL) was added, and the mixture was refluxed for 13 days. The solvent was then removed and the residue taken up in toluene. The solution was placed on a Florisil column and eluted with toluene. A greenish band shown by IR spectroscopy to contain **2** and the nickel species $Ni(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_4Me)_3$ eluted off the column. Purification attempts by recrystallization or selective extraction led to enrichment of **2**, but complete separation from $Ni(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_4Me)_3$ has not yet been achieved. Spectroscopic data for **2** are as follows. $^1$H NMR (chemical shifts at 10, −10, −30, and −50 °C, respectively, are given in brackets after the value at 20 °C): $\delta$ 5.16 [5.16, 5.18, 5.19, 5.20] (s, 5 H, $C_5H_5$), 4.30 [3.85, 3.15, 2.67, 2.20] (s, 9 H, $C_5H_4Me$), 1.25 [1.95, 2.86, 3.51, 4.13] (6 H, $C_5H_4Me$), 0.68 [1.28, 2.28, 2.98, 3.67] (6 H, $C_5H_4Me$). MS: $m/e$ = 658 ($M^+$), $(M - CO)^+$, $(M - 2CO)^+$, $(M - 2CO - 2C_5H_4Me)^+$. HRMS: calcd for $Ni_3MoC_{26}H_{26}O_3$, $m/e$ = 657.8996; found, $m/e$ = 657.8950. IR [$\nu$(CO)]: (Nujol) 1706 $cm^{-1}$ (thf) 1713 (s) $cm^{-1}$.

**Magnetic Studies.** The molar susceptibilities and magnetic moments of the clusters were determined by the $^1$H NMR method described by Evans.[17a] The low solubility and small magnetic moments of clusters **1a** and **1b** resulted in relatively large errors in the measurements and made corrections to the data, which are normally ignored, mandatory. Data were corrected for changes in density of the solvent with temperature;[17b] solutions of the clusters were prepared in chloroform, as this solvent's density at various temperatures has been reported.[21] The solution's density was assumed to be the same as that of chloroform at that temperature, a good approximation, as solution concentrations were $\leq 2 \times 10^{-2}$ M. The differing magnetic field strengths in the inner and outer tubes resulted in a ~2.5-Hz chemical shift difference for the solvent peak, and data were corrected for this. Adjustments were also made for the diamagnetism of the ligands[22] and chloroform.[23] Diamagnetic corrections for $Ni^+$ and $W^+$ were made by using known values for isoelectronic metal cations.[24] Values obtained are likely to be upper limits, as trace quantities of the paramagnetic cluster $Ni_3(\mu_3\text{-}CO)_2(\eta^5\text{-}C_5H_5)_3$ may be present, arising from decomposition of the clusters.

**X-ray Crystallography.** Black parallelepipeds of **1a** were grown from dichloromethane/hexane solutions. A crystal was transferred to the Picker four-circle diffractometer by using standard inert-atmosphere techniques employed at the Indiana University Molecular Structure Center and cooled to −155 °C. Full details of the diffractometry, low-temperature facilities, and computational procedures have been described.[25] A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to the space group $P2_12_12_1$; the subsequent solution and successful least-squares refinement confirmed this choice.

The structure was solved by a combination of direct methods (MULTAN 78) and Fourier techniques. Most of the hydrogen atoms were located in a difference Fourier synthesis; all hydrogen atoms were included as fixed-atom contributions (using idealized $sp^2$ and $sp^3$ geometry) in the final cycles of refinement. The correct enantiomer was chosen on the basis of the difference in residuals for the two possibilities. No absorption correction was deemed necessary, on the basis of several manual $\psi$ scans. The final difference Fourier was essentially featureless, the largest peak being ca. 1.0 e/Å$^3$.

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**Supplementary Material Available:** Tables of crystallographic data, bond distances and angles, and variation of magnetic moments with temperature and a plot of cyclopentadienyl $^1$H NMR chemical shifts versus temperature (7 pages); listings of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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