

Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization of Pure Research (ZWO, to A.L.S.)

**Registry No.** Ni(N-C-N)I, 84500-94-7; Ni(N-C-N)Br, 84500-93-6; Ni(N-C-N)Cl, 84500-92-5; Ni(N-C-N)NO<sub>2</sub>, 89618-53-1; Ni(N-C-N)NO<sub>3</sub>, 89618-54-2; Ni(N-C-N)N<sub>3</sub>, 89618-55-3; Ni(N-C-N)O<sub>3</sub>SCF<sub>3</sub>, 89618-56-4; [Ni(N-C-N)]<sub>2</sub>SO<sub>4</sub>, 89618-57-5; Ni(N-C-

N)OH, 89618-58-6; Ni(N-C-N)O<sub>2</sub>CH<sub>3</sub>, 89618-63-3; Ni(N-C-N)O<sub>2</sub>CMe, 89618-59-7; Ni(N-C-N)O<sub>2</sub>CPh, 89618-60-0; [Ni(N-C-N)H<sub>2</sub>O]BF<sub>4</sub>, 89618-62-2; (N-C-N)Br, 66479-06-9; [Ni(COD)]<sub>2</sub>, 1295-35-8.

**Supplementary Material Available:** Listings of observed and calculated structure factors for C<sub>13</sub>H<sub>20</sub>N<sub>2</sub>NiO<sub>2</sub> and positional and thermal parameters and bond distances and angles (21 pages). Ordering information is given on any current masthead page.

## Complexes [Mo(N<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub> and [Mo(CNR)(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (R = *n*-Butyl and *tert*-Butyl) Containing Bridging η<sup>1</sup>,η<sup>6</sup>-Triphenylphosphine Ligands. The Molecular Structure of [Mo(μ-η<sup>1</sup>,η<sup>6</sup>-PPh<sub>3</sub>)(PPh<sub>3</sub>)(CN(CH<sub>2</sub>)<sub>3</sub>Me)]<sub>2</sub>

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Received December 6, 1983

The reaction of tris(acetylacetonato)molybdenum with excess triphenylphosphine and triethylaluminum in toluene under nitrogen yields insoluble [Mo(μ-η<sup>1</sup>,η<sup>6</sup>-PPh<sub>3</sub>)(N<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub>·2C<sub>6</sub>H<sub>6</sub>. The structural assignment is based on the spectroscopic characterization (<sup>1</sup>H, <sup>31</sup>P, and <sup>13</sup>C NMR and IR) of soluble alkyl isocyanide derivatives of the dinitrogen complex [Mo(μ-η<sup>1</sup>,η<sup>6</sup>-PPh<sub>3</sub>)(CNR)(PPh<sub>3</sub>)<sub>2</sub>] (R = *n*-butyl, *tert*-butyl). The *n*-butyl isocyanide complex crystallizes in the space group *P* $\bar{1}$  with cell dimensions *a* = 15.141 (2) Å, *b* = 15.300 (3) Å, *c* = 16.912 (3) Å, α = 63.50 (2)°, β = 80.14 (1)°, γ = 79.37 (2)°, *V* = 3428 Å<sup>3</sup>, and *D*<sub>calcd</sub> = 1.36 g cm<sup>-3</sup> for *Z* = 2. The structure was solved by the heavy-atom method and refined by least-squares and Fourier methods to final residuals *R* = 0.0588 (*R*<sub>w</sub> = 0.0650) for 4147 observed (*I* > 3σ(*I*)) reflections. The complex is binuclear (symmetry *C*<sub>1</sub>) and racemic with respect to the chiral molybdenum centers. Averaged principal dimensions are Mo-P = 2.465 (3), Mo-C(ring) = 2.29 (2), Mo-C(isocyanide) = 1.96 (2), C-N = 1.18 (1), and Mo-Mo = 4.804 (1) Å. The isocyanide ligands have different C-N-C angles (155 (1)°, 163 (1)°) because they occupy axial and equatorial positions, respectively, on a Mo-C-P-Mo-C-P cyclohexane-like ring.

### Introduction

Studies of the reactions of dinitrogen coordinated in tertiary phosphine complexes of molybdenum(0) have provided much chemical information of relevance to the action of the nitrogen-fixing enzyme nitrogenase<sup>1</sup> and to the design of homogeneous catalysts<sup>2</sup> and electrocatalysts<sup>3</sup> for nitrogen fixation. The first dinitrogen complex of molybdenum(0) to be reported<sup>4</sup> was prepared by the reduction of tris(acetylacetonato)molybdenum (Mo(acac)<sub>3</sub>) with triethylaluminum in a concentrated solution of triphenylphosphine in an arene solvent under nitrogen. If the solvent was toluene, then an insoluble orange complex of formula Mo(N<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>·PhMe (1), ν(N<sub>2</sub>) = 2005 cm<sup>-1</sup>, was obtained in 13% yield. Similar compounds Mo-

(N<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub> were obtained by using benzene or mesitylene, and these were postulated to be polynuclear.<sup>4</sup> The structure of complex 1 was thought to be Mo(η<sup>6</sup>-PhMe)(N<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub> (2),<sup>1b,5</sup> although Green and Silverthorn obtained complex 2, ν(N<sub>2</sub>) = 1970 cm<sup>-1</sup>, by using a different synthetic route and showed that the properties of 2 differed from those reported for 1.<sup>6</sup> We have studied a variety of molybdenum(0) complexes containing η<sup>6</sup>-arylphosphine ligands including Mo(η<sup>6</sup>-PhPMePh)(L)-(PMePh)<sub>2</sub> (3a, L = N<sub>2</sub>, ν(N<sub>2</sub>) = 1980 cm<sup>-1</sup>, and 3b, L = CNCMe<sub>3</sub>, ν(CN) = 1940 cm<sup>-1</sup>) and suspected that complex 1 was a member of this structural class<sup>8,9</sup> with a unique

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dimeric structure.

### Experimental Section

**General Data.** All manipulations were carried out under an atmosphere of pure nitrogen. Toluene and tetrahydrofuran (THF) were dried over sodium-benzophenone and distilled under nitrogen. Methanol was dried over and distilled from magnesium methoxide. Complex 1 was prepared according to the literature method.<sup>4</sup> The NMR spectra were recorded by using a Varian XL-200 spectrometer. <sup>31</sup>P NMR spectra referenced to 85% H<sub>3</sub>PO<sub>4</sub> were recorded at 81 MHz and <sup>13</sup>C NMR, at 50.3 MHz, using this machine. Microanalyses were performed on samples handled under an inert atmosphere by the Canadian Microanalytical Service, Vancouver.

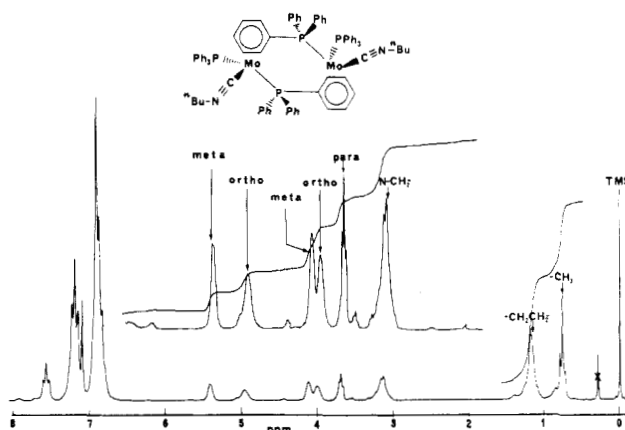
**Preparation of [Mo(μ-η<sup>6</sup>-PPh<sub>3</sub>)(CN-*n*-Bu)(PPh<sub>3</sub>)<sub>2</sub>] (4a).** *n*-Butyl isocyanide (22.4 μL, 0.27 mmol) was added to a suspension of [Mo(N<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub>·2PhMe (1, 0.20 g, 0.13 mmol) in 10 mL of THF. Nitrogen was evolved rapidly, and a clear orange solution was produced. The orange product was obtained by concentrating the solution to 2 mL in vacuo and then adding methanol (4 mL). It was recrystallized from THF/methanol: yield, 0.16 g, 90%; IR (Nujol) 2000–1800 cm<sup>-1</sup> (b, NC); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 8.0–6.8 (m, 50 H, PhPMo), 5.45 (m, 2 H meta, η<sup>6</sup>-Ph), 4.99 (m, 2 H ortho, η<sup>6</sup>-Ph), 4.15 (m, 2 H meta, η<sup>6</sup>-Ph), 4.04 (m, 2 H ortho, η<sup>6</sup>-Ph), 3.75 (t, *J* = 5.3 Hz, 2 H para, η<sup>6</sup>-Ph), 3.16 (m, 4 H, CH<sub>2</sub>N≡C), 1.19 (m, 8 H, MeCH<sub>2</sub>CH<sub>2</sub>), 0.77 (m, 6 H, CH<sub>3</sub>); <sup>31</sup>P NMR (C<sub>6</sub>H<sub>6</sub>) δ 56.7 (A), 62.8 (B) (AB pattern, *J*<sub>AB</sub> = 28.1 Hz); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>) δ 211.6 (dd, *J*<sub>CP</sub> = 16, 18 Hz, 2 C, MoCN), 140.7 (d, *J* = 27 Hz, 2 C-P, PhP-η<sup>6</sup>-Ph), 135.1 (d, *J* = 11 Hz, 1 C-P, PhP-η<sup>6</sup>-Ph), 134.3 (d, *J* = 12 Hz, 6 C-P, Ph<sub>3</sub>PMo), 132.6 (d, *J* = 9 Hz, 1 C-P, PhP-η<sup>6</sup>-Ph), 129.1–126.9 (m, 20 C ortho + 20 C meta + 10 C para, PhPMo), 88.6 (d, *J* = 14 Hz, 2 C-P, η<sup>6</sup>-Ph), 84.0 (m, 4 C meta, η<sup>6</sup>-Ph), 82.8 (d, *J* = 10 Hz, 2 C ortho, η<sup>6</sup>-Ph), 74.9 (d, *J* = 5 Hz, 2 C ortho, η<sup>6</sup>-Ph), 71.1 (m, 2 C para, η<sup>6</sup>-Ph), 46.0 (s, 2 C, CH<sub>2</sub>N), 33.2 (s, 2 C, CCN), 20.3 (s, 2 C, CCCN), 13.9 (s, 2, CH<sub>3</sub>). Anal. Calcd for C<sub>82</sub>H<sub>78</sub>N<sub>2</sub>P<sub>4</sub>Mo<sub>2</sub>: C, 69.98; H, 5.59; N, 1.99. Found: C, 69.86; H, 5.62; N, 1.91. Molecular weight determinations for complex 4a (*M*<sub>r</sub>, 1407) in benzene were consistently low; the Signer method<sup>10</sup> using complex 3b<sup>7d</sup> as the standard gave *M*<sub>r</sub>, 1130 ± 50; osmometry (Analytische Laboratorien, Engelskirchen) gave *M*<sub>r</sub>, 710. Complex 4b was not soluble enough for these studies.

**Preparation of [Mo(μ-η<sup>6</sup>-PPh<sub>3</sub>)(CN-*t*-Bu)(PPh<sub>3</sub>)<sub>2</sub>] (4b).** The preparation of 4a was followed but *tert*-butyl isocyanide was used: yield 90%; IR (Nujol) 2000–1800 cm<sup>-1</sup> (b, NC); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 8.0–6.8 (m, 50 H, PhP), 5.11 (m, 2 H meta, η<sup>6</sup>-Ph), 4.99 (m, 2 H ortho, η<sup>6</sup>-Ph), 4.23 (m, 2 H meta, η<sup>6</sup>-Ph), 3.92 (m, 2 H ortho + 2 H para, η<sup>6</sup>-Ph), 1.00 (s, 18 H, Me<sub>3</sub>C); <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>) δ 59.3 (A), 54.7 (B) (AB pattern, *J*<sub>AB</sub> = 28 Hz). Anal. Calcd for C<sub>82</sub>H<sub>78</sub>N<sub>2</sub>P<sub>4</sub>Mo<sub>2</sub>: C, 69.98; H, 5.59; N, 1.99. Found: C, 69.77; H, 5.70; N, 1.86.

**Crystallographic Analysis of Complex 4a.** Orange crystals, obtained by slow evaporation of a THF/methanol solution, were wedged into 0.2–0.3-mm Lindemann capillaries and sealed under nitrogen. A crystal of dimensions 0.10 × 0.23 × 0.28 mm was used throughout. Precession photographs were used to obtain preliminary cell and symmetry information. Further work on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.71069 Å) gave the following crystal data.

**Crystal Data.** C<sub>82</sub>H<sub>78</sub>Mo<sub>2</sub>N<sub>2</sub>P<sub>4</sub> is triclinic, of space group *P*1̄ with *a* = 15.141 (2) Å, *b* = 15.300 (3) Å, *c* = 16.912 (3) Å, α = 63.50 (2)°, β = 80.14 (1)°, γ = 79.37 (2)°, *U* = 3428 Å<sup>3</sup>, and *D*<sub>calc</sub> = 1.36 g cm<sup>-3</sup> for *Z* = 2; Mo Kα radiation (λ = 0.71069 Å), μ(Mo Kα) = 4.8 cm<sup>-1</sup>.

Cell constants were obtained by least-squares refinement of the setting angles of 25 reflections (8.1 < θ < 16.5°). Intensity data were collected in the θ:2θ mode with scan ranges of (0.85 +



**Figure 1.** The <sup>1</sup>H NMR spectrum at 200 MHz of *rac*-4a in C<sub>6</sub>D<sub>6</sub>. The η<sup>6</sup>-arene peaks in the region δ 3–6 (inset) have been assigned by decoupling studies. Small unassigned peaks may be due to *meso*-4a.

0.35 tan θ)° within a maximum scan time of 75 s. All 9905 reflections in the quadrants *h*, ±*k*, ±*l* with 2θ ≤ 45° were collected. Three standard reflections, which were monitored after every 12000 s of exposure time, showed a gradual loss in intensities over the period of the data collection. Other conditions were the same as ref 7d.

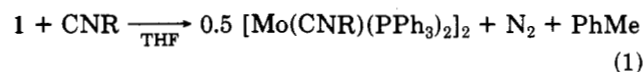
After Lorentz and polarization corrections were applied, the data were rescaled on the basis of the intensities of the standard reflections (maximum rescale factor 1.404). Subsequent averaging of equivalent reflections and the rejection of reflections with *F*<sub>o</sub> = 0.0 gave a final data set of 7668 reflections.

The structure was solved by the use of the Patterson function to locate the two Mo atoms. All other atoms were then located after several cycles of least-squares and Fourier calculations, and in the final cycles hydrogen atoms were placed in calculated positions (C–H = 0.95 Å; B = 7 Å<sup>2</sup>) but were not refined. Full-matrix least-squares refinement minimizing ∑w||*F*<sub>o</sub> – |*F*<sub>c</sub>||<sup>2</sup> then converged (maximum shift/error = 0.09) to the agreement indices *R*<sub>1</sub> = 0.0588 (*R*<sub>w</sub> = 0.0650) for 4147 observed (*I* > 3σ(*I*)) reflections (Mo and P atoms with anisotropic thermal parameters). Two reflections (1,0,0) and (0,1,1) with large ωΔ<sup>2</sup> and unsymmetrical backgrounds in the initial data collection were rejected from the final refinement cycles. In the final cycle, weights were given by *w* = 4/*F*<sup>2</sup>{σ(*I*)<sup>2</sup> + (0.05*F*<sup>2</sup>)<sup>2</sup>}<sup>-1</sup>, and, at convergence, the esd of an observation of unit weight was 1.39. The final difference Fourier contained as its major features several residual peaks up to 0.55 e Å<sup>-3</sup> close to the Mo atoms. A PDP 11/23 computer and programs in the Enraf-Nonius SDP package were used for the refinements.

Final positional parameters for non-hydrogen atoms and selected bond lengths and bond angles are given in Tables I–III. Tables IV–VIII containing supplementary crystallographic data have been deposited (see below).

### Results and Discussion

In order to resolve the question of the structure of 1, we prepared new, soluble isocyanide derivatives of 1 as orange, air-sensitive solids of formulae Mo(CNR)(PPh<sub>3</sub>)<sub>2</sub> (4a, R = *n*-butyl; 4b, R = *tert*-butyl), according to reaction 1 in 90% yield. The <sup>1</sup>H NMR spectra of complexes 4 clearly



indicated the presence of an η<sup>6</sup>-PhPPh<sub>2</sub> ligand by the presence of five resonances in the region δ 3–6 due to inequivalent arene protons on the π-complexed ring. Figure 1 shows the assignment of the peaks for complex 4a as determined by selective decoupling experiments. The most shielded ortho and meta protons likely lie nearest the phenyl groups of the σ-bonded triphenylphosphine ligand. The two phosphorus nuclei on each

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Table I. Positional Parameters and Their Estimated Standard Deviations<sup>a</sup>

atom	x	y	z	B, Å <sup>2</sup>	atom	x	y	z	B, Å <sup>2</sup>
Mo1	0.21295 (7)	0.38035 (6)	0.40952 (6)	2.56 (2)	C224	-0.1239 (9)	0.5118 (9)	0.1902 (8)	5.5 (3)*
Mo2	0.31892 (7)	0.58138 (6)	0.10786 (6)	2.75 (2)	C225	-0.0948 (9)	0.5346 (9)	0.2502 (8)	5.8 (3)*
P1	0.1444 (2)	0.2341 (2)	0.5211 (2)	3.36 (8)	C226	-0.0071 (8)	0.4969 (8)	0.2756 (7)	4.7 (3)*
P2	0.1627 (2)	0.3844 (2)	0.2763 (2)	2.62 (7)	C231	0.2357 (7)	0.4455 (7)	0.1750 (6)	2.5 (2)*
P3	0.3533 (2)	0.5814 (2)	0.2447 (2)	3.01 (8)	C232	0.3309 (7)	0.4148 (7)	0.1778 (6)	2.8 (2)*
P4	0.2401 (2)	0.7487 (2)	0.0298 (2)	3.71 (9)	C233	0.3881 (8)	0.4426 (7)	0.0977 (7)	3.6 (3)*
N12	0.3848 (7)	0.2360 (6)	0.3954 (6)	4.8 (2)	C234	0.3545 (8)	0.5070 (7)	0.0151 (7)	3.6 (3)*
N22	0.5046 (7)	0.6675 (7)	0.0278 (6)	4.9 (2)*	C235	0.2638 (7)	0.5402 (7)	0.0114 (7)	3.3 (2)*
C11	0.3180 (8)	0.2881 (7)	0.4020 (7)	3.5 (3)*	C236	0.2037 (7)	0.5110 (7)	0.0915 (6)	2.9 (2)*
C13	0.466 (1)	0.173 (1)	0.423 (1)	7.9 (4)*	C311	0.3593 (8)	0.7002 (7)	0.2491 (7)	3.5 (3)*
C14	0.467 (1)	0.129 (1)	0.525 (1)	13.0 (7)*	C312	0.4000 (8)	0.7703 (8)	0.1759 (7)	4.4 (3)*
C15	0.459 (1)	0.198 (1)	0.568 (1)	11.5 (6)*	C313	0.403 (1)	0.8623 (9)	0.1751 (8)	6.0 (3)*
C16	0.518 (2)	0.253 (2)	0.515 (2)	23 (1)*	C314	0.367 (1)	0.8802 (9)	0.2459 (9)	6.4 (4)*
C21	0.4330 (8)	0.6409 (7)	0.0585 (7)	4.0 (3)*	C315	0.3248 (9)	0.8132 (9)	0.3170 (8)	5.8 (3)*
C23	0.578 (1)	0.724 (1)	-0.0051 (9)	7.4 (4)*	C316	0.3202 (9)	0.7206 (8)	0.3198 (7)	4.9 (3)*
C24	0.640 (1)	0.696 (1)	0.063 (1)	10.2 (5)*	C321	0.2806 (7)	0.5220 (7)	0.3464 (6)	3.2 (2)*
C25	0.717 (2)	0.760 (1)	0.030 (1)	13.8 (7)*	C322	0.1849 (7)	0.5466 (7)	0.3424 (6)	3.1 (2)*
C26	0.690 (2)	0.858 (2)	0.011 (1)	14.8 (8)*	C323	0.1230 (8)	0.5155 (7)	0.4208 (7)	3.5 (3)*
C111	0.0274 (7)	0.2265 (7)	0.5128 (7)	3.4 (2)*	C324	0.1566 (8)	0.4550 (7)	0.5011 (7)	3.9 (3)*
C112	-0.0039 (8)	0.1399 (8)	0.5275 (7)	4.7 (3)*	C325	0.2485 (8)	0.4289 (7)	0.5090 (7)	3.6 (3)*
C113	-0.0926 (9)	0.1423 (8)	0.5125 (8)	5.3 (3)*	C326	0.3090 (8)	0.4596 (7)	0.4320 (7)	3.7 (3)*
C114	-0.1500 (9)	0.2281 (9)	0.4853 (8)	5.6 (3)*	C331	0.4697 (8)	0.5244 (7)	0.2774 (7)	3.9 (3)*
C115	-0.1191 (8)	0.3140 (8)	0.4724 (7)	4.8 (3)*	C332	0.5175 (9)	0.4608 (8)	0.2458 (8)	5.0 (3)*
C116	-0.0310 (8)	0.3131 (8)	0.4849 (7)	4.1 (3)*	C333	0.606 (1)	0.4177 (9)	0.2654 (8)	6.5 (4)*
C121	0.1381 (8)	0.2226 (7)	0.6351 (7)	3.6 (3)*	C334	0.645 (1)	0.441 (1)	0.3188 (9)	7.2 (4)*
C122	0.2165 (9)	0.2040 (8)	0.6708 (8)	5.1 (3)*	C335	0.600 (1)	0.502 (1)	0.3525 (9)	7.0 (4)*
C123	0.217 (1)	0.1934 (9)	0.7578 (8)	6.3 (4)*	C336	0.5089 (9)	0.5457 (9)	0.3334 (8)	6.0 (3)*
C124	0.139 (1)	0.203 (1)	0.8042 (9)	7.4 (4)*	C411	0.1414 (8)	0.7543 (7)	-0.0246 (7)	3.7 (3)*
C125	0.060 (1)	0.226 (1)	0.7714 (9)	6.8 (4)*	C412	0.0661 (8)	0.7173 (8)	0.0297 (7)	4.1 (3)*
C126	0.0569 (8)	0.2363 (8)	0.6819 (7)	4.7 (3)*	C413	-0.0124 (9)	0.7191 (8)	-0.0038 (8)	4.9 (3)*
C131	0.1964 (7)	0.1063 (7)	0.5425 (6)	3.4 (2)*	C414	-0.0144 (9)	0.7630 (8)	-0.0947 (8)	5.2 (3)*
C132	0.2394 (8)	0.0861 (7)	0.4739 (7)	3.8 (3)*	C415	0.059 (1)	0.800 (1)	-0.1488 (9)	7.0 (4)*
C133	0.2793 (8)	-0.0062 (7)	0.4857 (7)	3.9 (3)*	C416	0.1376 (9)	0.7973 (9)	-0.1150 (8)	5.4 (3)*
C134	0.2786 (8)	-0.0811 (8)	0.5700 (7)	4.7 (3)*	C421	0.1848 (8)	0.8403 (7)	0.0725 (7)	4.0 (3)*
C135	0.2379 (9)	-0.0633 (9)	0.6386 (8)	5.8 (3)*	C422	0.1768 (8)	0.8146 (8)	0.1613 (7)	4.8 (3)*
C136	0.1943 (9)	0.0291 (8)	0.6269 (8)	5.2 (3)*	C423	0.132 (1)	0.8820 (9)	0.1961 (8)	6.3 (4)*
C211	0.1638 (7)	0.2663 (7)	0.2709 (6)	3.2 (2)*	C424	0.092 (1)	0.9719 (9)	0.1392 (9)	6.5 (4)*
C212	0.0905 (7)	0.2145 (7)	0.3142 (6)	3.4 (3)*	C425	0.098 (1)	0.9971 (9)	0.0516 (9)	6.5 (4)*
C213	0.0926 (8)	0.1193 (8)	0.3181 (7)	4.6 (3)*	C426	0.1418 (9)	0.9334 (8)	0.0164 (8)	5.2 (3)*
C214	0.1628 (8)	0.0786 (8)	0.2820 (7)	4.6 (3)*	C431	0.3182 (8)	0.8227 (8)	-0.0662 (7)	4.7 (3)*
C215	0.2371 (9)	0.1291 (8)	0.2397 (8)	5.3 (3)*	C432	0.357 (1)	0.7864 (9)	-0.1259 (8)	6.2 (4)*
C216	0.2360 (8)	0.2234 (7)	0.2334 (7)	3.9 (3)*	C433	0.426 (1)	0.833 (1)	-0.194 (1)	8.0 (4)*
C221	0.0506 (7)	0.4404 (7)	0.2391 (6)	3.0 (2)*	C434	0.447 (1)	0.912 (1)	-0.195 (1)	9.8 (5)*
C222	0.0173 (8)	0.4230 (8)	0.1761 (7)	4.5 (3)*	C435	0.413 (1)	0.955 (1)	-0.142 (1)	9.3 (5)*
C223	-0.0695 (9)	0.4595 (9)	0.1510 (8)	5.7 (3)*	C436	0.344 (1)	0.908 (1)	-0.0709 (9)	7.0 (4)*

<sup>a</sup> Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as  $(\text{Å}^2/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$ .

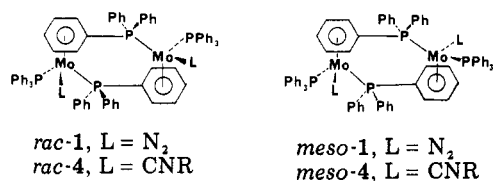
Table II. Bond Distances (Å)<sup>a</sup>

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Mo1	P1	2.463 (3)	P1	C111	1.829 (10)	C15	C16	1.28 (3)
Mo1	P2	2.472 (3)	P1	C121	1.843 (10)	C23	C24	1.47 (2)
Mo1	C11	1.949 (10)	P1	C131	1.863 (10)	C24	C25	1.53 (2)
Mo1	C321	2.297 (9)	P2	C211	1.845 (9)	C25	C26	1.39 (2)
Mo1	C322	2.265 (9)	P2	C221	1.833 (10)	C231	C232	1.433 (12)
Mo1	C323	2.322 (9)	P2	C231	1.826 (9)	C231	C236	1.423 (12)
Mo1	C324	2.280 (10)	P3	C311	1.870 (10)	C232	C233	1.411 (12)
Mo1	C325	2.290 (10)	P3	C321	1.821 (10)	C233	C234	1.417 (12)
Mo1	C326	2.231 (10)	P3	C331	1.872 (11)	C234	C235	1.375 (12)
Mo2	P3	2.458 (3)	P4	C411	1.854 (10)	C235	C236	1.433 (12)
Mo2	P4	2.474 (3)	P4	C421	1.856 (10)	C321	C322	1.435 (12)
Mo2	C21	1.980 (11)	P4	C431	1.874 (11)	C321	C326	1.421 (12)
Mo2	C231	2.359 (9)	N12	C11	1.188 (11)	C322	C323	1.429 (12)
Mo2	C232	2.267 (9)	N12	C13	1.421 (14)	C323	C324	1.379 (12)
Mo2	C233	2.255 (10)	N22	C21	1.180 (12)	C324	C325	1.387 (13)
Mo2	C234	2.262 (10)	N22	C23	1.421 (15)	C325	C326	1.400 (13)
Mo2	C235	2.310 (10)	C13	C14	1.56 (2)			
Mo2	C236	2.326 (9)	C14	C15	1.50 (2)			

<sup>a</sup> Numbers in parentheses are estimated standard deviations in the least significant digits.

molybdenum were shown to be inequivalent by <sup>31</sup>P NMR and by <sup>13</sup>C NMR where two couplings <sup>2</sup>J<sub>CP</sub> to the metal-bonded isocyanide carbon were observed. These features

were consistent with racemic or meso stereoisomers I or II which contain bridging η<sup>1</sup>,η<sup>6</sup>-PPh<sub>3</sub> ligands in the configuration observed previously for [Cr(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub>.<sup>9a</sup>



These spectra also showed that each compound **4** was produced in only one configuration from reaction **2** and that compounds derived from complex **2** were not present.

A single-crystal X-ray structure determination of complex **4a** was carried out to determine the nuclearity and stereochemistry of the complexes. The crystal contained discrete binuclear molecules of symmetry  $C_1$  with a form of structure I (*rac*) where the six-membered Mo1–C321–P3–Mo2–C231–P2 ring is in a flattened chair conformation (Figures 2 and 3) with Mo1 and Mo2 0.716 (1) and 0.529 (1) Å, respectively, out of the P2,P3,C231,C321 plane. The terminal  $\sigma$ -bonded triphenylphosphine ligands occupy an equatorial site at Mo1 and an axial site at Mo2 in this cyclohexane-like ring. The 4.804 (1)-Å Mo–Mo separation is too great for a significant metal–metal interaction.

The  $\eta^1, \eta^6$ -PPh<sub>3</sub> ligands have very similar dimensions to comparable  $\eta^6$ -bonded arylphosphines in mononuclear complexes, suggesting that the ligands can bridge between the metals without significant strain. For example the Mo–C(ring) distances in **4a** (2.23 (1)–2.36 (1) Å, average 2.29 Å), **3b** (average 2.28 Å) and Mo( $\eta^6$ -PhPMe<sub>2</sub>)(PMe<sub>2</sub>Ph)<sub>3</sub><sup>8c</sup> (average 2.28 Å) are similar. The bridging phosphorus atoms P2 and P3 are displaced out of the best plane defined by the  $\eta^6$ -arene ring to which each is attached and away from Mo2 and Mo1, respectively, by 0.362 (3) and 0.234 (3) Å, respectively. The phosphorus or arsenic substituent on  $\eta^6$ -bonded ligands in mononuclear or binuclear complexes are typically located *exo* to the metal with respect to the ring with comparable displacements from the plane of the ring (0.2–0.4 Å).<sup>7d,8c,9c,d</sup> By contrast strain is induced in a related ligand that is forced to bridge the manganese–molybdenum bond in the complex (CO)<sub>4</sub>MnMo(CO)<sub>3</sub>[ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>].<sup>11</sup> This is indicated by long Mo–C(ring) distances and a bending down of the phosphorus atom from the plane of the cyclopentadiene ring toward the manganese atom by 0.42 Å.<sup>11</sup>

The average molybdenum–phosphorus distance of 2.465 (3) Å is longer than that found in the mononuclear analogue **3b** (2.418 (3) Å) which has smaller, more basic PPh<sub>2</sub> ligands.<sup>7d</sup> However, it is shorter than the average Mo–P distance of 2.577 (2) Å observed for *cis*-Mo-(PPh<sub>3</sub>)<sub>2</sub>(CO)<sub>4</sub> which contains more electron-withdrawing ligands.<sup>12</sup> The wide angles P–Mo–P of the latter complex (104.62 (7)°) and of complex **4a** (P3–Mo2–P4 = 103.1 (1)°; P1–Mo1–P2 = 97.9 (1)°) result from steric interactions between bulky *cis* ligands. These interactions are expressed in the crystal structure of **4a** as intramolecular distances between atoms on adjacent ligands that are equal to or shorter than typical van der Waals' contacts (2.1–3.4 Å); these are listed in Table VI (supplementary material). There are more close contacts between phenyls on *cis* phosphorus atoms P1 and P2 (between rings 11 and 21, 13 and 21, and 11 and 22) than between those on P3 and P4 (between rings 31 and 42 only). There are other differences in interligand contacts around Mo1 compared to

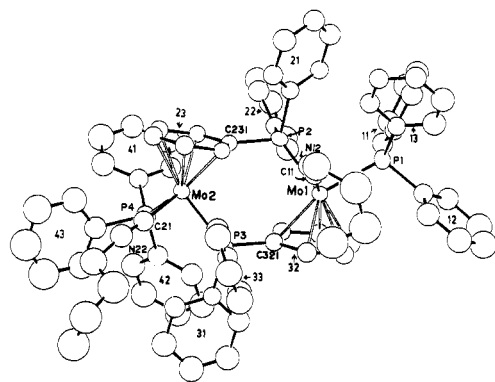


Figure 2. Molecular structure of **4a** showing the numbering of selected atoms and phenyl rings.

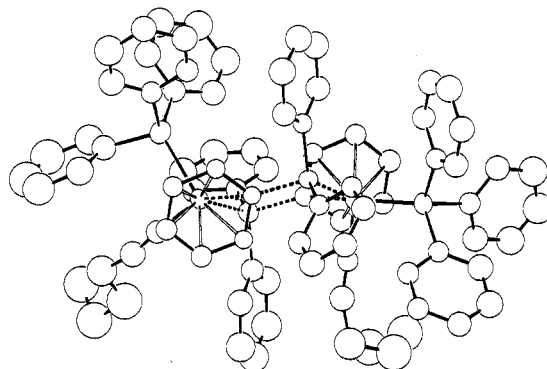


Figure 3. The molecular structure of **4a** viewed at right angles to the  $\eta^6$ -bonded rings showing the chair conformation of the Mo–P–C–Mo–P–C ring.

those around Mo2, and together these account for the irregularities in dimensions of the cyclohexane-like ring: the bond Mo1–P2 (2.472 (3) Å) is longer than the bond Mo2–P3 (2.458 (3) Å); and the corresponding angles Mo–P–C and Mo–C–P in the MoPCMoPC ring are different. In addition the distance from Mo1 to the best plane through ring 32 (1.794 (1) Å) is shorter than that from Mo2 to ring 23 (1.807 (1) Å); the metal atoms are not exactly centered on these rings and the Mo–C(ring) distances show more variation than comparable distances in complexes **3b** and Mo( $\eta^6$ -PhPMe<sub>2</sub>)(PMe<sub>2</sub>Ph)<sub>3</sub>.

As in other electron-rich isocyanide complexes,<sup>7d,13</sup> the *n*-butyl isocyanide ligands in **4a** are bent at the nitrogen and have short Mo–C bonds due to  $\pi$ -back-bonding from the metal. The CNC angles for the two are different (155 (1) and 163 (1)°) as are the Mo–C distances (1.95 (1) and 1.98 (1) Å) because the ligands occupy axial and equatorial positions at Mo1 and Mo2, respectively, on the cyclohexane-like ring discussed above. A comparable CNC angle of 150 (1)° and Mo–C distance of 1.98 (1) Å are observed for mononuclear **3b**.

Richards and Pombeiro have studied reactions involving substitution of isocyanide for dinitrogen ligands in a variety of complexes.<sup>13a,14</sup> The reactions are stereoselective, implying that isocyanide ligands have similar stereochemical requirements to dinitrogen. Complex **1** exists in only one form in the solid state according to its infrared spectrum

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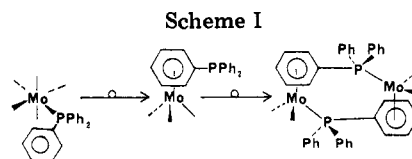
Table III. Bond Angles (deg)<sup>a</sup>

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
P1	Mo1	P2	98.0 (1)	C231	Mo2	C233	64.2 (3)	Mo2	C231	P2	139.5 (5)
P1	Mo1	C11	85.8 (3)	C231	Mo2	C234	76.1 (3)	Mo2	C231	C232	68.5 (5)
P1	Mo1	C321	161.3 (3)	C231	Mo2	C235	64.4 (3)	Mo2	C231	C236	71.0 (5)
P1	Mo1	C322	141.5 (3)	C231	Mo2	C236	35.4 (3)	P2	C231	C232	117.1 (7)
P1	Mo1	C323	106.3 (3)	C232	Mo2	C233	36.4 (3)	P2	C231	C236	124.2 (1)
P1	Mo1	C324	87.4 (3)	C232	Mo2	C234	65.9 (3)	C232	C231	C236	118.2 (9)
P1	Mo1	C325	96.0 (3)	C232	Mo2	C235	76.8 (3)	Mo2	C232	C231	75.5 (5)
P1	Mo1	C326	126.8 (3)	C232	Mo2	C236	64.5 (3)	Mo2	C232	C233	71.3 (6)
P2	Mo1	C11	89.7 (3)	C233	Mo2	C234	36.6 (3)	C231	C232	C233	119.3 (9)
P2	Mo1	C321	100.1 (3)	C233	Mo2	C235	64.1 (4)	Mo2	C233	C232	72.3 (6)
P2	Mo1	C322	85.9 (3)	C233	Mo2	C236	75.3 (4)	Mo2	C233	C234	72.1 (6)
P2	Mo1	C323	101.5 (3)	C234	Mo2	C235	35.0 (3)	C232	C233	C234	121.3 (9)
P2	Mo1	C324	134.1 (3)	C234	Mo2	C236	63.9 (4)	Mo2	C234	C233	71.4 (6)
P2	Mo1	C325	161.9 (3)	C235	Mo2	C236	36.0 (3)	Mo2	C234	C235	74.4 (6)
P2	Mo1	C326	134.4 (3)	Mo1	P1	C111	117.5 (3)	C233	C234	C235	120 (1)
C11	Mo1	C321	98.8 (4)	Mo1	P1	C121	112.8 (3)	Mo2	C235	C234	70.7 (6)
C11	Mo1	C322	132.7 (4)	Mo1	P1	C131	122.6 (3)	Mo2	C235	C236	72.6 (6)
C11	Mo1	C323	161.9 (4)	C111	P1	C121	101.9 (5)	C234	C235	C236	119.7 (9)
C11	Mo1	C324	136.2 (4)	C111	P1	C131	100.5 (5)	Mo2	C236	C231	73.6 (6)
C11	Mo1	C325	102.7 (4)	C121	P1	C131	98.1 (4)	Mo2	C236	C235	71.4 (6)
C11	Mo1	C326	86.1 (4)	Mo1	P2	C211	118.2 (3)	C231	C236	C235	121.1 (9)
C321	Mo1	C322	36.6 (3)	Mo1	P2	C221	123.2 (3)	P3	C311	C312	117.0 (8)
C321	Mo1	C323	65.5 (4)	Mo1	P2	C231	113.0 (3)	P3	C311	C316	122.9 (9)
C321	Mo1	C324	76.7 (4)	C211	P2	C221	97.7 (5)	Mo1	C321	P3	134.8 (5)
C321	Mo1	C325	65.3 (4)	C211	P2	C231	99.6 (4)	Mo1	C321	C322	70.5 (6)
C321	Mo1	C326	36.6 (3)	C221	P2	C231	101.3 (4)	Mo1	C321	C326	69.3 (6)
C322	Mo1	C323	36.3 (3)	Mo2	P3	C311	120.2 (3)	P3	C321	C322	117.5 (7)
C322	Mo1	C324	64.1 (4)	Mo2	P3	C321	118.0 (3)	P3	C321	C326	126.5 (8)
C322	Mo1	C325	76.0 (3)	Mo2	P3	C331	115.2 (4)	C322	C321	C326	115.8 (9)
C322	Mo1	C326	65.1 (4)	C311	P3	C321	100.7 (5)	Mo1	C322	C321	72.9 (5)
C323	Mo1	C324	34.9 (3)	C311	P3	C331	95.9 (5)	Mo1	C322	C323	74.0 (6)
C323	Mo1	C325	63.4 (4)	C321	P3	C331	103.4 (5)	C321	C322	C323	121.6 (9)
C323	Mo1	C326	75.9 (4)	Mo2	P4	C411	114.7 (3)	Mo1	C323	C322	69.7 (5)
C324	Mo1	C325	35.3 (3)	Mo2	P4	C421	130.3 (4)	Mo1	C323	C324	71.0 (6)
C324	Mo1	C326	64.3 (4)	Mo2	P4	C431	108.6 (4)	C322	C323	C324	119 (1)
C325	Mo1	C326	36.0 (3)	C411	P4	C421	94.9 (5)	Mo1	C324	C323	74.2 (6)
P3	Mo2	P4	103.1 (1)	C411	P4	C431	102.8 (5)	Mo1	C324	C325	72.7 (6)
P3	Mo2	C21	82.9 (3)	C421	P4	C431	101.9 (5)	C323	C324	C325	122 (1)
P3	Mo2	C231	97.7 (2)	C11	N12	C13	156 (1)	Mo1	C325	C324	72.0 (6)
P3	Mo2	C232	88.6 (2)	C21	N22	C23	163 (1)	Mo1	C325	C326	69.7 (6)
P3	Mo2	C233	109.5 (3)	Mo1	C11	N12	176.5 (9)	C324	C325	C326	119 (1)
P3	Mo2	C234	145.1 (3)	N12	C13	C14	112 (1)	Mo1	C326	C321	74.2 (6)
P3	Mo2	C235	162.0 (3)	C13	C14	C15	118 (2)	Mo1	C326	C325	74.2 (6)
P3	Mo2	C236	127.5 (3)	C14	C15	C16	98 (2)	C321	C326	C325	123 (1)
P4	Mo2	C21	86.7 (3)	Mo2	C21	N22	172.9 (9)	P3	C331	C332	120.2 (9)
P4	Mo2	C231	119.6 (2)	N22	C23	C24	112 (1)	P3	C331	C336	121.5 (9)
P4	Mo2	C232	155.1 (3)	C23	C24	C25	112 (2)	P4	C411	C412	117.2 (8)
P4	Mo2	C233	146.4 (3)	C24	C25	C26	114 (2)	P4	C411	C416	124.3 (9)
P4	Mo2	C234	109.9 (3)	P1	C111	C112	123.5 (8)	P4	C421	C422	119.6 (8)
P4	Mo2	C235	86.9 (3)	P1	C111	C116	117.6 (8)	P4	C421	C426	121.8 (8)
P4	Mo2	C236	91.3 (2)	P1	C121	C122	117.8 (9)	P4	C431	C432	119 (1)
C21	Mo2	C231	152.4 (4)	P1	C121	C126	121.9 (9)	P4	C431	C436	120 (1)
C21	Mo2	C232	116.8 (4)	P1	C131	C132	119.9 (8)				
C21	Mo2	C233	89.5 (4)	P1	C131	C136	122.6 (8)				
C21	Mo2	C234	87.7 (4)	P2	C211	C212	117.4 (7)				
C21	Mo2	C235	113.0 (4)	P2	C211	C216	123.8 (8)				
C21	Mo2	C236	149.0 (4)	P2	C221	C222	121.4 (8)				
C231	Mo2	C232	36.0 (3)	P2	C221	C226	121.8 (9)				

<sup>a</sup> Numbers in parentheses are estimated standard deviations in the least significant digits.

which displays only one sharp dinitrogen absorption. Thus **1** likely also has the *rac* configuration **I**. The reaction of **1** with carbon monoxide may not be as stereoselective as the isocyanide reactions because products with two carbonyl absorptions ( $\nu(\text{CO}) = 1800$  and  $1820 \text{ cm}^{-1}$ ) sometimes form.<sup>4b</sup>

Hidai et al. reported that the bis(dinitrogen) complex  $\text{Mo}(\text{N}_2)_2(\text{dppe})_2$ ,  $\text{dppe} = \text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2$ , forms under reaction conditions similar to that used to prepare **1**.<sup>4</sup> The unknown complex  $\text{Mo}(\text{N}_2)_2(\text{PPh}_3)_4$  may be an intermediate on the way to complex **1** since a large excess of triphenylphosphine is required in the reaction;<sup>4</sup> however, this bis(dinitrogen) compound is expected to be unstable due to steric crowding among the bulky phosphine ligands.<sup>15</sup>



The smaller methylidiphenylphosphine ligands in *trans*- $\text{Mo}(\text{N}_2)_2(\text{PMePh}_2)_4$  are known to be labile because of steric

(15) A similar complex,  $\text{RuH}_2(\text{PPh}_3)_4$ , rearranges in the presence of acid to  $[\text{Ru}(\eta^6\text{-PhPPh}_2)(\text{H})(\text{PPh}_3)_2]\text{BF}_4$ ; (a) McConway, J. C.; Skapski, A. C.; Phillips, L.; Young, R. J.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* 1974, 327. (b) Cole-Hamilton, D. J.; Young, R. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* 1976, 1995.

repulsions, and this complex readily rearranges under vacuum to the  $\pi$ -complex  $\text{Mo}(\eta^6\text{-PhPMePh})(\text{PMePh}_2)_3$ .<sup>16</sup> The latter complex also contains a labile  $\sigma$ -bonded ligand that is substituted by dinitrogen.<sup>7a</sup> A parallel sequence of reactions (Scheme I) for the bulkier triphenylphosphine system could explain the formation of compound 1.

The recent discovery that two molybdenum(0) centers are required to reduce one dinitrogen ligand to ammonia<sup>1c,17</sup> makes the protonation reactions of binuclear dinitrogen complexes of which 1 is a rare example<sup>18,19</sup> of special interest. We are currently trying to make soluble binuclear dinitrogen complexes starting from 1 in order

to investigate their reactions with strong acids.

**Acknowledgment.** This work was supported by an operating grant to R.H.M. and a grant for the diffractometer from the Natural Sciences and Engineering Research Council of Canada.

**Note Added in Proof.** We recently discovered that complex 1, when still damp with toluene after being filtered from its mother liquor, is soluble enough in tetrahydrofuran to obtain its <sup>31</sup>P NMR spectrum at 81 MHz:  $\delta$  62.4 (A), 48.0 (B) (AB pattern,  $J_{AB} = 28$  Hz). This spectrum is consistent with the *rac* structure proposed for 1.

**Registry No.** 1, 89773-11-5; 4a, 89746-31-6; 4b, 89746-32-7.

**Supplementary Material Available:** Tables of calculated hydrogen atom positions (Table IV), bond lengths and bond angles in the phenyl rings (Table V), inter- and intraligand contacts within van der Waals' distances (Table VI), and final thermal parameters (Table VII) and a listing of structure factor amplitudes (Table VIII) (45 pages). Ordering information is given on any current masthead page.

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## Study of the Reactivity of [Fe<sub>2</sub>(CO)<sub>6</sub>(μ-CO)(μ-C(C<sub>6</sub>H<sub>5</sub>)C(C<sub>6</sub>H<sub>5</sub>)H)]<sup>-</sup> toward the CH<sub>3</sub>OC(O)C≡CC(O)OCH<sub>3</sub> and CF<sub>3</sub>C≡CCF<sub>3</sub> Alkynes. Crystal Structure of the Products Resulting from Two Different Modes of Combination of the Alkynes with the Bridging Ligands [Fe<sub>2</sub>(CO)<sub>6</sub>(μ-C(C(O)OCH<sub>3</sub>)C(C(O)OCH<sub>3</sub>)C(O)C(C<sub>6</sub>H<sub>5</sub>)C(C<sub>6</sub>H<sub>5</sub>)H)]<sup>-</sup> and [Fe<sub>2</sub>(CO)<sub>6</sub>(μ-C(C<sub>6</sub>H<sub>5</sub>)C(C<sub>6</sub>H<sub>5</sub>)C(CF<sub>3</sub>)C(CF<sub>3</sub>)H)]<sup>-</sup>

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Received December 12, 1983

[Fe<sub>2</sub>(CO)<sub>6</sub>(μ-CO)(μ-C(C<sub>6</sub>H<sub>5</sub>)C(C<sub>6</sub>H<sub>5</sub>)H)]<sup>-</sup> was reacted with RC≡CR alkynes (R = CH<sub>3</sub>OC(O), CF<sub>3</sub>) affording [Fe<sub>2</sub>(CO)<sub>6</sub>(μ-C(R)C(R)C(O)C(C<sub>6</sub>H<sub>5</sub>)C(C<sub>6</sub>H<sub>5</sub>)H)]<sup>-</sup> (R = CH<sub>3</sub>OC(O) (3), CF<sub>3</sub> (5)) and [Fe<sub>2</sub>(CO)<sub>6</sub>(μ-C(C<sub>6</sub>H<sub>5</sub>)C(C<sub>6</sub>H<sub>5</sub>)C(R)C(R)H)]<sup>-</sup> (R = CF<sub>3</sub> (4)). The structure of 3 and 4 has been determined by single-crystal X-ray crystallography. Complex 3 crystallizes in the space group *P*2<sub>1</sub>/*n* with *Z* = 4 and lattice constants *a* = 17.244 (6) Å, *b* = 23.419 (7) Å, *c* = 12.218 (5) Å, and  $\beta = 94.31$  (4)°. This product results from the double insertion of carbon monoxide and alkyne into the Fe-C bond of the ethenyl ligand. Furthermore, the oxygen of the acyl group is bonded to a Fe atom. Complex 4 crystallizes in the space group *P* $\bar{1}$  with *Z* = 2 and lattice constants *a* = 15.397 (5) Å, *b* = 14.495 (4) Å, *c* = 11.258 (4) Å,  $\alpha = 107.35$  (3)°,  $\beta = 96.92$  (2)°, and  $\gamma = 110.85$  (3)°. This product results from the insertion of the alkyne into the carbon-hydrogen bond of the ethenyl ligand. Furthermore, the C(CF<sub>3</sub>)C(CF<sub>3</sub>)H fragment of the organic part of the molecule is  $\mu$ - $\eta^1$  bonded to the two iron atoms. A possible mechanism for the two types of insertion observed is proposed.

### Introduction

The study of the reactivity of organic molecules linked to dinuclear metal centers is presently an extensive field of interest.<sup>3,4</sup> In a recent publication<sup>5</sup> we have shown that

the anion [HFe<sub>3</sub>(CO)<sub>11</sub>]<sup>-</sup> reacts with diphenylacetylene at 60 °C giving two products: one in which the trinuclear iron

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