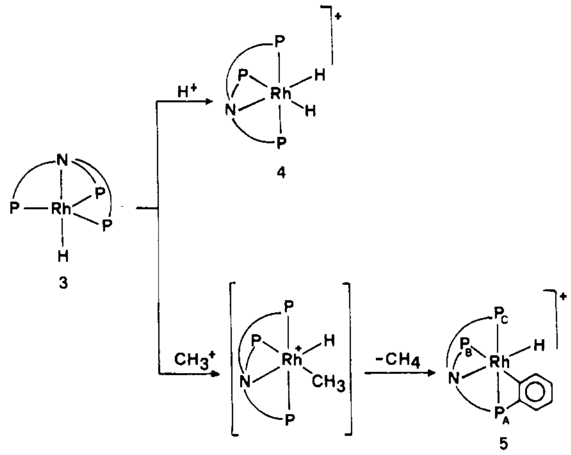
Organometallics 1986, *5*, 2559–2561 2559

Scheme II



substitution pattern of one of the phenyl groups of the ligand,[8] respectively. The ^{1}H NMR spectrum (TDF, 293 K) of **5** exhibits an unresolved multiplet at −11.5 ppm in the hydride region. The absence of J(H–P) values >20 Hz indicates that the hydride ligand lies trans to the nitrogen atom of np$_3$. Finally, the ^{31}P{^{1}H} NMR spectrum (C$_6$D$_6$, 293 K) consists of a typical ABCX pattern as expected for the obvious nonequivalence of the three phosphorus atoms of np$_3$. The ^{31}P NMR assignments[9] are as follows (see Scheme II): δ(P$_A$) 25.70 (J(P$_A$–P$_B$) = 22.6 Hz, J(P$_A$–P$_C$) = 436.1 Hz, J(P$_A$–Rh) = 104.3 Hz), δ(P$_B$) 12.95 (J(P$_B$–P$_C$) = 13.2 Hz, J(P$_B$–Rh) = 80.9 Hz), δ(P$_C$) −34.08 (J(P$_C$–Rh) = 74.8 Hz).

On the basis of the experimental evidence summarized in Scheme II, the complex [(np$_3$)RhH(Me)]$^+$ is the most likely product of the straightforward methylation of **3**. Evidently, under the conditions employed, such a cis methyl hydride is not stable and reductively eliminates CH$_4$ to give the 16-electron cis-unsaturated fragment [(np$_3$)Rh]$^+$. Finally, the latter species intramolecularly activates a phenyl C–H bond of the ligand to give **5**. Interestingly, the ortho-metalated derivative is obtained also when the reaction of **3** with MeSO$_3$CF$_3$ is carried out in the presence of COD.

At variance with the [(np$_3$)Rh]$^+$ fragment, the isoelectronic species [(np$_3$)Ir]$^+$ prefers to oxidatively add one sp^2 C–H bond of COD through an intermolecular process rather than to intramolecularly activate a phenyl C–H bond of the np$_3$ ligand. Such a metal dependence on C–H activation when all the other conditions are even is not unusual and may depend on steric,[1h] thermodynamic, and kinetic factors.[1e,10]

Registry No. **1**, 104910-88-5; **2**, 104910-94-3; **2**·CH$_3$COCH$_3$, 104910-95-4; **3**, 85233-91-6; **4**, 104910-90-9; **5**, 104910-92-1; np$_3$, 15114-55-3; [Ir(COD)Cl]$_2$, 12112-67-3; COD, 111-78-4.

Supplementary Material Available: Listings of final atomic parameters and bond lengths and angles (6 pages); a listing of observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

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[8] Ittel, S. D.; Tolman, C. A.; Krusic, P. J.; English, A. D.; Jesson, J. P. *Inorg. Chem.* **1978**, *17*, 3432.

[9] Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

[10] Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929.

Carbonylation of $(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_2H$

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Summary: The reaction of (η^6-C$_6$(CH$_3$)$_6$)Mn(CO)$_2$H (**1**) with CO at atmospheric pressure or 40 psi in THF, hexane, or acetone yields *endo*-(η^5-C$_6$H(CH$_3$)$_6$)Mn(CO)$_3$ (*endo*-**2**). This unusual result has been confirmed by determination of the molecular structure of *endo*-**2** by X-ray crystallography. Reaction of **1**, deuteriated at Mn–H, gives *endo*-**2** deuteriated in the exo position in acetone solution, but no deuterium tracing is found for the reaction in THF solution.

Although numerous unsuccessful attempts to insert carbon monoxide into metal–hydrogen bonds have been reported, there are two reports of metal formyls prepared from carbon monoxide and the corresponding metal hydride.[1,2] Evidence for an intermediate formyl complex, formed in a similar manner, by a metal hydride has been reported.[3] The carbonylation study reported here was undertaken to determine if (η^6-C$_6$(CH$_3$)$_6$)Mn(CO)$_2$H (1)[4] would form a stable metal formyl or proceed to product formation through a metal formyl intermediate.

The reaction of P(C$_6$H$_5$)$_3$ with (η^6-C$_6$H$_6$)Mn(CO)$_2$CH$_3$ leads to migration of methyl from manganese to arene giving the endo-methylated η^5-cyclohexadienyl product.[5] In this reaction the acyl (η^6-C$_6$H$_6$)Mn(CO)(P(C$_6$H$_5$)$_3$,(C(O)CH$_3$) has been identified as an equilibrium participant.[6] This observation suggests that carbonylation of 1 might lead to the formation of a metal formyl which could be involved as an equilibrium participant or intermediate in the formation of *exo*-(η^5-C$_6$H(CH$_3$)$_6$)Mn(CO)$_3$ (*exo*-2). Conversely the formation of a metal formyl would not be expected to play a role in any intramolecular mechanism which would lead to the formation of *endo*-2.

The carbonylation experiments were performed at 25 °C by using dilute rigorously deoxygenated solutions of 1 (10–20 mM) in THF, acetone, or hexane. Carbon monoxide was either bubbled through the solution at atmospheric pressure, or the glass reaction vessel was pressurized to 40 psi. The progress of the reaction was followed by recording the IR spectra of samples removed from the reaction mixture. An induction period in excess of 1 h was always observed during which the concentration of 1 decreased slightly, but no *endo*-2 was formed. The length of the induction period was observed to decrease with

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[1] (OEP)Rh(CHO) is formed from CO and (OEP)RhH. (a) Wayland, B. B.; Woods, B. A. *J. Chem. Soc., Chem. Commun.* **1981**, 700. (b) Wayland, B. B.; Woods, B. A. *J. Am. Chem. Soc.* **1982**, *104*, 302.

[2] (C$_5$Me$_5$)ThH(OR) addds CO to form the η^2-formyl derivative. Fagan, P. J.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6959.

[3] (η-C$_5$H$_5$)Fe[(C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$](CHO) is formed as an intermediate by hydride migration to CO. Davies, S. G.; Simpson, S. J. *J. Organomet. Chem.* **1982**, *240*, C48.

[4] (a) Bernhardt, R. J.; Eyman, D. P. *Organometallics* **1984**, *3*, 1445. (b) Bernhardt, R. J.; Wilmoth, M. A.; Weers, J. J.; LaBrush, D. M.; Eyman, D. P.; Huffman, J. C. *Organometallics* **1986**, *5*, 883.

[5] Brookhart, M.; Pinhas, A. R.; Lukacs, A. *Organometallics* **1982**, *12*, 1730.

[6] Brookhart, M., private communication.

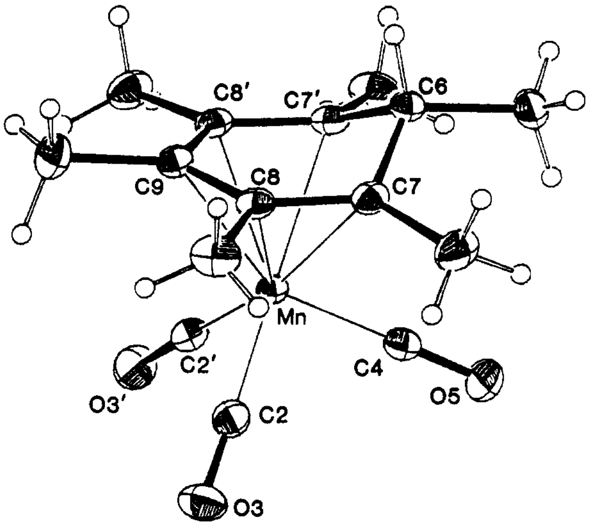


Figure 1. ORTEP drawing for *endo*-(η^5-$C_6H(CH_3)_6$)Mn(CO)$_3$.

Table I. Selected Bond Lengths and Bond Angles for *endo*-(η^5-$C_6H(CH_3)_6$)Mn(CO)$_3$

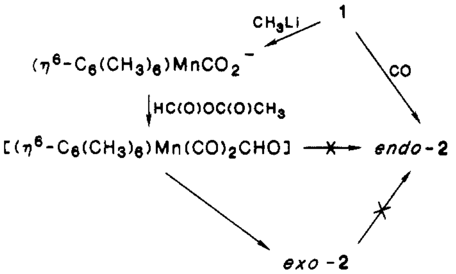
	Bond Lengths (Å)		
Mn-C(2)	1.8019 (17)	C(6)-H(1)	0.99 (3)
Mn-C(4)	1.8039 (25)	C(6)-C(7)	1.5267 (22)
Mn-C(7)	2.2308 (16)	C(7)-C(8)	1.4144 (22)
Mn-C(8)	2.1533 (16)	C(8)-C(9)	1.4350 (20)
Mn-C(9)	2.1509 (23)	C(6)-C(10)	1.528 (3)
C(2)-O(3)	1.1518 (21)		
C(4)-O(5)	1.153 (3)		
	Bond Angles (deg)		
Mn-C(2)-O(3)	178.06 (15)	C(7)-C(8)-C(9)	119.04 (16)
Mn-C(4)-O(5)	179.55 (20)	C(6)-C(7)-C(8)	116.97 (15)
C(2)-Mn-C(2')	86.87 (11)	C(7)-C(6)-C(7')	103.33 (18)
C(2)-Mn-C(4)	95.12 (7)	C(7)-C(6)-C(10)	113.84 (13)
C(2)-Mn-C(8)	88.87 (7)	C(7)-C(6)-H(1)	110.1 (9)
C(8)-C(9)-C(8')	118.74 (20)	C(10)-C(6)-H(1)	105.8 (16)

increasing concentration of 1. The rate of the reaction, after the induction period, displayed no change with variation of CO pressure and was the same when CP or research grade CO was used. The initial concentration of 1 had no pronounced influence on the reaction rate. During the reaction the CO bands of 1[7] disappeared while new bands, at 1995 and 1916 cm^{-1}, grew in. In THF the reaction required approximately 6 h to proceed to completion as determined by IR. The reaction was slower in acetone and hexane. In methanol no reaction was observed in 24 h. After solvent removal by vacuum evaporation, the product was isolated and purified by vacuum sublimation.

The yellow crystalline product displayed the melting point, and the ^{1}H NMR and IR spectra previously reported for *endo*-2[8–10] In addition its mass spectrum displayed a molecular ion peak. The IR spectrum of the product was not unequivocal in establishing the isomer identity since the bands previously assigned to CO stretching modes for *endo*-2 and its exo isomer differ by only ~2.0 cm^{-1}.[10,11]

The molecular structure of the carbonylation product was determined by single-crystal X-ray analysis.[12] The crystals used were obtained by slow evaporation of a THF solution. The structure of 1, shown in the ORTEP drawing (Figure 1), is similar to that of the non-methylated analogue (η^5-C_6H_7)Mn(CO)$_3$[13] in that it involves a "piano-stool" structure with a η^5-cyclohexadienyl attached to a manganese tricarbonyl unit. The molecule lies on a crystallographic mirror plane, and the carbonyls are eclipsed with C(6), C(8), and C(8') of the cyclohexadienyl ring. Table I gives some pertinent bond lengths and angles. This X-ray structure verifies the ^{1}H NMR spectral assignments found in the literature for *endo*-2 and *exo*-2[8,9] and establishes that the product of carbonylation of 1 is *endo*-2.

Scheme I



The possible role of the metal formyl (η^6-$C_6(CH_3)_6$)Mn(CO)$_2$CHO as an intermediate in the formation of *exo*-2 is eliminated by the results of a study of the reaction of the conjugate base of 1 with formic acetic anhydride at 25 °C in THF. The anion (η^6-$C_6(CH_3)_6$)Mn(CO)$_2^-$,[4] formed by deprotonation of 1 with CH$_3$Li, reacts very rapidly on mixing with HC(O)OC(O)CH$_3$ to give *exo*-2 as a solution species and solid lithium acetate.[14] The established reaction of metal anions with formic acetic anhydride to produce metal formyls[15] suggests that this observation is consistent with an intramolecular rearrangement of the initially formed metal formyl which is an intermediate in the formation of *exo*-2, as shown in Scheme I.

Since the carbonylation product *endo*-2 is not the one expected from intramolecular hydride migration, steps were taken to determine if the expected product *exo*-2 could be converted to *endo*-2 under the conditions of the reaction. It was observed that *exo*-2 does not react with carbon monoxide in THF in 6 h. Thermolysis and photolysis of THF solutions of *exo*-2 produced no *endo*-2 but did lead to some decomposition. These results suggest that *endo*-2 is not formed from the isomerization of initially formed *exo*-2 but is the actual product of the reaction between carbon monoxide and 1. These conclusions are summarized in Scheme I.

Carbonylation of (η^6-$C_6(CH_3)_6$)Mn(CO)$_2$D[16] (1-*d*) in THF resulted in formation of *endo*-2 with no deuterium in the product, whereas in acetone the product contains only deuterium in the exo position. The interpretation of these results is complicated by the observation that in THF solution neither 1-*d*, nor *endo*-2, deuteriated in the *exo*-

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[7] Spectral properties: IR (ν_{CO}, THF) 1939, 1883 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 2.35 (s 18 H), -10.9 (s, 1 H).

[8] Munro, G. A. M.; Pauson, P. L. *Isr. J. Chem.* **1976**, *15*, 258.

[9] Winkhaus, G.; Pratt, L.; Wilkinson, G. W. *J. Chem. Soc.* **1961**, 3807.

[10] Spectral properties for *endo*-(η^5-$C_6H(CH_3)_6$)Mn(CO)$_3$: IR (ν_{CO}, THF) 1995, and 1916 cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.96 (m, 1 H), 2.05 (s, 3 H), 1.66 (s, 6 H), 1.28 (s, 6 H), 1.11 (d, 3 H).

[11] Spectral properties for *exo*-(η^5-$C_6H(CH_3)_6$)Mn(CO)$_3$: IR (ν_{co} THF) 1993 cm^{-1} and 1914 cm^{-1}; ^{1}H NMR (C_6D_6) δ 2.24 (m, 1 H), 2.05 (s, 3 H), 1.63 (s, 6 H), 1.45 (s, 6 H), 0.13 (d, 3 H).

[12] Crystal data: $C_{15}H_{19}O_3Mn$, yellow color, space group $P2_1/m$, a = 8.227 (1) Å, b = 9.172 (1) Å, c = 9.917 (2) Å, β = 107.44°, Z = 2, density = 1.406 g/cm^3; 1745 unique reflections. The structure was solved by direct methods and Fourier techniques and refined by full-matrix least squares. The final residuals were $R(F)$ = 0.027 and $R_w(F)$ = 0.030. All hydrogen atoms were visible in a difference Fourier phased on the nonhydrogen paramters and were included in the final cycles. The molecule lies on a crystallographic mirror plane.

[13] Churchill, M. R.; Scholer, F. R. *Inorg. Chem.* **1969**, *8*, 1950.

[14] *exo*-2 was identified by ^{1}H NMR and IR (see ref 11) and lithium acetate was identified by IR.

[15] (a) Collman, J. P.; Winter, S. R. *J. Am. Chem. Soc.* **1976**, *95*, 4089. (b) Fiato, R. A.; Vidal, J. L.; Pruett, R. L. *J. Organomet. Chem.* **1979**, *172*, C4. (c) Heinz, B.; Weiler, G. *Angew, Chem., Int. Ed. Engl.* **1982**, *21*, 150.

[16] See ref 4. Compound 1-*d* was prepared by using the same technique used in the synthesis of 1 but with NaBD$_4$.

position (*endo*-2-*d*), undergo exchange with THF in the time required for the carbonylation of 1 to proceed to completion. In addition no deuterium kinetic isotope effect is observed when 1-*d* is carbonylated in THF to give *endo*-2.

From the results presented here, it is concluded that the reaction between 1 and CO proceeds by a mechanism different from the intramolecular mechanism proposed for the reaction of (η^6-C_6H_6)Mn$(CO)_2CH_3$ and $P(C_6H_5)_3$.[5] In THF the reaction apparently does not involve direct intermolecular transfer of hydride from 1 because carbonylation of 1-*d* leads to the formation of no *endo*-2-*d*. This conclusion is consistent with the absence of a deuterium kinetic isotope effect. Since neither 1-*d* nor *endo*-2-*d* exchanges with THF during the reaction period, the formation of product, by hydride ion or hydrogen atom transfer from 1 to the exo position in the product, would be expected to display deuterium tracing and a deuterum kinetic isotope effect when 1-*d* is used. The observations in THF suggest that an undetected intermediate or intermediates, probably of very low concentration, are involved in product formation. A detailed FTIR study, designed to identify intermediates and to establish the mechanism of this reaction, is in progress.

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Registry No. 1, 91230-53-4; *endo*-2, 65700-52-9.

Supplementary Material Available: Stereoviews, tables of crystal data, anisotropic thermal parameters, and fractional coordinates and isotropic thermal parameters, and complete listings of bond lengths and bond angles (6 pages); a listing of observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

Binuclear Metallapyrrolidone Complexes Formed from Coupling of CO and Alkynes with the μ_3-Nitrene Ligand of $Ru_3(\mu_3\text{-NPh})(CO)_{10}$

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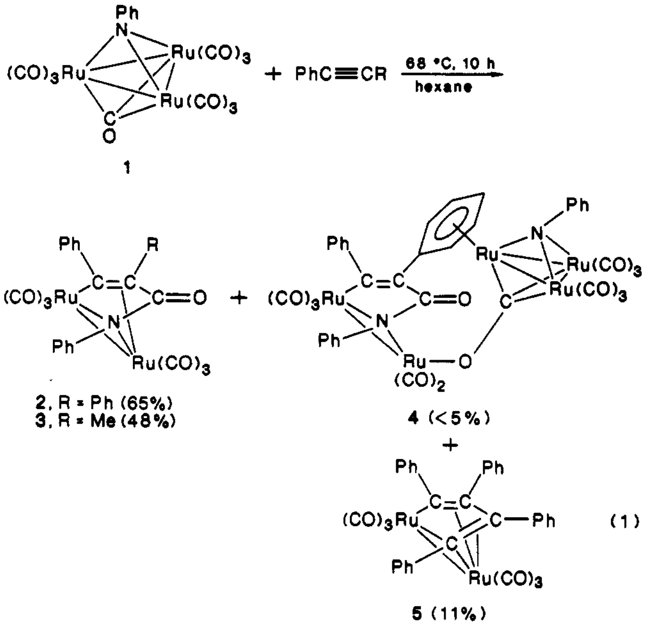
Summary: The μ_3-nitrene cluster **1** reacts with PhC≡CPh to give the binuclear metallapyrrolidone complex **2** formed by combination of the alkyne with CO and the nitrene ligand. This species further reacts with PhC≡CPh and CO to form pentaphenylpyridone and 1,3,4-triphenylmaleimide, respectively. Low-yield products accompanying the synthesis of **2** are the metallacyclopentadiene complex **5** and the unusual Ru_5 cluster **4**. The structures of **2** and **4** have been crystallographically established.

The chemistry of low-valent metal carbene complexes has been extensively investigated and many such compounds have found impressive synthetic utility.[1] In contrast, the chemistry of nitrene ligands bound to low-valent metals remains relatively unexplored,[2] even though such ligands have been invoked as intermediates in several catalytic reactions.[3] In our efforts to develop the chemistry of μ_3-nitrene ligands in metal clusters, we previously demonstrated the coupling of nitrenes with carbene and acyl ligands to give imidates,[4] carbamates,[5] and benzanilide.[5] Herein we report the first examples of coupling of μ_3-nitrenes with alkynes and CO to give binuclear metallapyrrolidone complexes from which pyridones and imides subsequently derive.

The metallapyrrolidone complex 2[6] forms in good yield when the μ_3-nitrene cluster 1[7] is heated in the presence of PhC≡CPh (eq 1). Complex 2 has been crystallographically characterized (Figure 1).[8] The Ru atoms of 2 are



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(3) (a) Cenini, S.; Pizzotti, M.; Crotti, C.; Porta, F.; Monica, G. L. *J. Chem. Soc., Chem. Commun.* **1984**, 1286. (b) Alper, H.; Hashem, K. E. *J. Am. Chem. Soc.* **1981**, *103*, 6515. (c) L'eplattenier, F.; Matthys, P.; Calderazzo, F. *Inorg. Chem.* **1970**, *9*, 342. (d) Andrew, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1979**, *101*, 7225. (e) Dawoodi, Z.; Mays, M. J.; Henrick, K. *J. Chem. Soc., Dalton Trans.* **1984**, 433. (f) Bhaduri, S.; Gopalkrishnan, K. S.; Clegg, W.; James, P. G.; Sheldrick, G. M.; Stalke, D. *J. Chem. Soc., Dalton Trans.* **1984**, 1765. (g) Bernhardt, W.; Schnering, V. C.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 279.

(4) Williams, G. D.; Geoffroy, G. L.; Whittle, R. R.; Rheingold, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 729.

(5) Williams, G. D.; Geoffroy, G. L.; Rheingold, A. L., to be submitted for publication.

(6) 2: IR (hexane) ν_{CO} 2091 (m), 2066 (vs), 2020 (vs), 2002 (s), 1717 (m) cm^{-1}; *m/z* (EI) 669; ^1H NMR (CD_2Cl_2) δ 7.26 (br, Ph). Anal. Calcd: C, 56.04; H, 2.74. Found: C, 55.89; H, 2.70.

(7) (a) Bhaduri, S.; Gopalkrishnan, K. S.; Sheldrick, G. M.; Clegg, W.; Stalke, D. *J. Chem. Soc., Dalton Trans.* **1983**, 2339. (b) For an improved preparation from $Ru_3(CO)_{12}$ and PhNO see: Smieja, J. A.; Gladfelter, W. L. *Inorg. Chem.* **1986**, *25*, 2667.

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