Organometallics **1986,** *5,* 894-898

studies show that colorless benzene-d_6 solutions of 3 under vacuum in sealed tubes are stable at room temperature but heating them above 40 °C results in red-brown solutions whose NMR spectra bear only the signals of the starting material. Further studies are in progress to investigate the thermal decomposition and other reactions of 3.

Summary

The metathesis of $Li[(C_6H_5)_2P(C_5H_4)]$ with $ZrCl_4{\cdot}2THF$ in benzene offers a convenient, high yield synthesis of the metallo ligand 1. This complex readily reacts with $(C_7H_8)Mo(CO)_4$ to give 2. NMR spectroscopy shows no strong interactions of the two metals other than some small but significant shifts in proton and phosphorus resonances (downfield). Infrared data suggest that 1 and similar complexes where the diphenylphosphine moeity is atached to the Cp ring will behave (at least spectroscopically) as triphenylphosphines or chelating bis(diphenylphosphino)alkanes. The crystal structure of 2 shows very little distortion about the coordination spheres of the two metals which is consistent with a lack of strong interactions between the metals. However, the chelating metallo ligand 1 binds the molybdenum atom nearly 0.6 Å closer than the nonbonded single phosphine bridged Ti–Mn system. The chlorides bonded to the zirconium atom in 2 are readily exchanged for methyl groups using methylmagnesium bromide. These spectroscopic and structural data suggest that this functionalized sandwich juxtaposes the two metals without significantly altering their physical and chemical properties. Studies are in progress to investigate the spectroscopic, electrochemical, and chemical properties of 3 and similar heterobinuclear complexes derived from 1 and 2.

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Registry No. 1, 100898-54-2; 2, 100898-55-3; $[(C_6H_5)_2P(C_5H_4)]_2Zr(CH_3)_2Mo(CO)_4$, 100898-56-4; $Li[(C_6H_5)_2P(C_5H_4)]$, 83272-80-4; $ZrCl_4{\cdot}2THF$, 21959-01-3; (norbornadiene)tetracarbonylmolybdenum(0), 12146-37-1.

Supplementary Material Available: Tables of refined thermal parameters, the carbon–hydrogen distances and angles, the pertinent least-squares planes, and calculated and observed structure factor amplitudes (27 pages). Ordering information is given on any current masthead page.

Reaction of $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(THF)$ with $PhCH_2N_3$ To Yield Binuclear $(\eta^5\text{-}CH_3C_5H_4)_2Mn_2(CO)_3[\mu\text{-}C(O)N(CH_2Ph)N_2]$, an Intermediate in the Formation of Benzyl Isocyanate

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The reaction of benzyl azide with $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(THF)$ results in the formation of $(\eta^5\text{-}CH_3C_5H_4)_2Mn_2(CO)_3[\mu\text{-}C(O)N(CH_2Ph)N_2]$ (1). The structure of 1 has been established by an X-ray diffraction study. It crystallizes in the space group $P2_1/n$ with a = 7.2175 (8) Å, b = 14.3614 (17) Å, c = 21.2811 (20) Å, β = 99.531 (9)°, V = 2175.4 (3) Å^3, and Z = 4. The structure refined to $R_F = 0.0449$ and $R_{wF} = 0.0476$ for the 2826 reflections with $F_o \geqslant 3\sigma(F_o)$. Each Mn is coordinated by a $\eta^5\text{-}CH_3C_5H_4$ ligand and by a CO. The Mn–Mn bond (2.777 (1) Å) is bridged by the $\mu\text{-}C(O)N(CH_2Ph)N_2$ ligand and by a weakly semibridging CO (Mn(1)–C(3) = 2.608 (5) Å). Complex 1 is photoactive, producing $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(THF)$ and $PhCH_2NCO$ when irradiated in THF solution. Irradiation of methanol solutions of 1 produces methyl *N*-benzylcarbamate. The entire reaction sequence represents the stepwise carbonylation of benzyl azide to benzyl isocyanate proceeding through a stable binuclear intermediate.

Recent studies have indicated that triply bridging nitrene ligands in metal clusters have an interesting derivative chemistry. The coupling of μ_3-NR ligands with carbenes,[1a] acyls,[1b] and hydrides[2] is now documented. These μ_3-NAr ligands have also been proposed as key intermediates in the homogeneous catalyzed reduction of nitroaromatics by $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ to yield carbamates and other organics.[3] Nitrene-containing metal clusters are clearly in need of further study, but one problem that may limit the development of their chemistry is the scarcity of compounds which contain μ_3-NR ligands and the lack of general, high-yield synthetic routes to them.[4]

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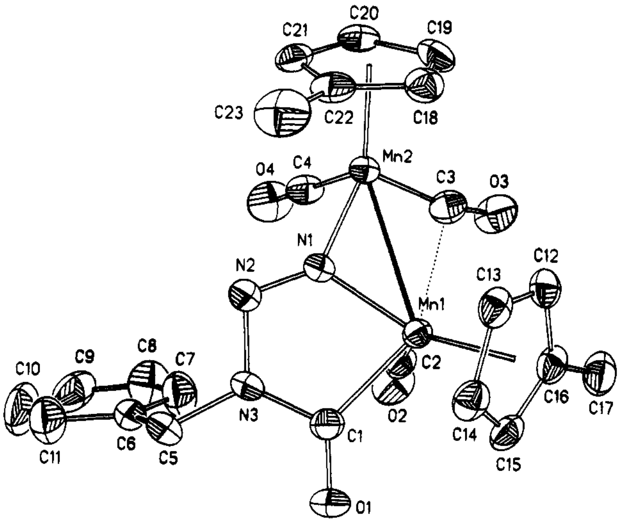
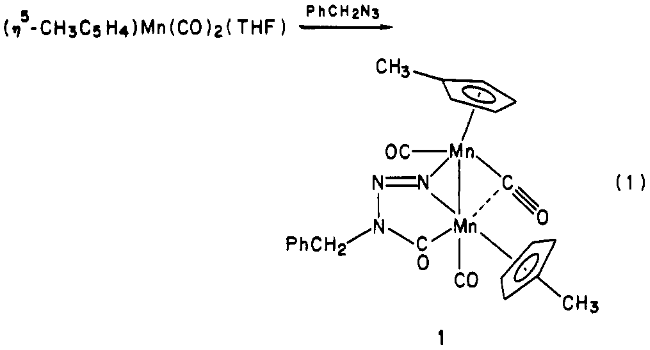


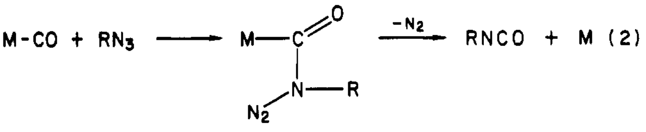
Figure 1. Molecular structure and labeling scheme for $Mn_2C_{23}H_{21}N_3O_4$. Atoms are depicted at the 50% probability level.

One potential route to μ_3-NR capped clusters is the reaction of organic azides with coordinatively unsaturated metal carbonyls with loss of N_2 and assembly of the metal fragments around the incipient nitrene. This route has been used for the preparation of Fe_3 and Os_3 clusters containing μ_3-NR ligands,[5] but it has not been generally employed. We wished to extend this methodology to other metals and accordingly examined the reaction of $PhCH_2N_3$ with $(MeCp)Mn(CO)_2(THF)$, anticipating the formation of a $Mn_3(\mu_3\text{-NR})$ cluster. However, as reported herein this reaction does not produce μ_3-NCH_2Ph compounds but rather azide–carbonyl coupling to give the binuclear complex 1 (eq 1).



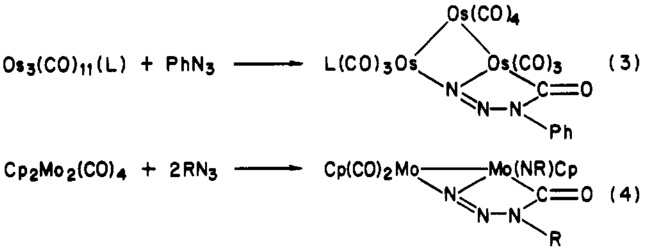
1

The reaction of azides with CO is an interesting reaction because it can potentially lead to isocyanates and isocyanate-derived products. The uncatalyzed reaction of organic azides with carbon monoxide yields isocyanates only at elevated temperatures and CO pressure.[6] However, these reactions are catalyzed by transition metal complexes so that the reactions proceed under much milder conditions (e.g., 1 atm of CO, 45 °C, $RhCl(CO)(PPh_3)_2$ catalyst).[7] The mechanism of the azide to isocyanate conversion has not been fully detailed. However, it has been suggested that it involves the attack of the azide on a CO ligand to give an intermediate such as A followed by N_2 loss and decoordination of the RNCO ligand (eq 2).[8]



A

Although intermediates such as A have been proposed for reactions of azides with metal carbonyls, they have never been observed in mononuclear complexes, although they do form with polynuclear complexes. The reactive ligand in A can be stabilized by bridging of the terminal nitrogen between two metals as evidenced by the two examples shown in eq 3 and 4.[9] However, the conversion of these bridging μ-$C(O)N(R)N_2$ ligands to the corresponding isocyanates has not been established. Herein we show that the μ-$C(O)N(CH_2Ph)N_2$ ligand in complex 1 readily loses N_2 to give the free isocyanate when irradiated in THF solution. Mononuclear $(\eta^5\text{-}CH_3C_5H_4)Mn$ complexes are formed in this latter reaction, and the overall sequence constitutes a cycle in which mononuclear complexes convert an azide into an isocyanate via the intermediacy of a binuclear species.



Results

Reaction of $PhCH_2N_3$ with $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(THF)$. Addition of $PhCH_2N_3$ to $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(THF)$, generated photochemically from $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3$ in THF solution, initially gave a purple solution whose infrared spectrum indicated only the presence of $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(THF)$ and $PhCH_2N_3$. However, concentration of this solution by solvent removal under vacuum at 0 °C gave a dark green oil. An IR spectrum of this oil dissolved in CH_2Cl_2 showed the presence of $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3$, $PhCH_2N_3$, and new ν_{CO} absorbances at 1972, 1925, 1885, and 1607 cm^{-1}. Silica gel chromatography gave first a light yellow band of $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3$ with $PhCH_2N_3$ followed by a green band of $(\eta^5\text{-}CH_3C_5H_4)_2Mn_2(CO)_3[\mu\text{-}C(O)N(CH_2Ph)N_2]$ (1). Complex 1 was isolated in 17% recrystallized yield. Although the overall yield of 1 is low, IR spectroscopy indicates that the only other organometallic product is $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3$. Red crystals of 1 are air-stable, although green solutions of 1 have proven slightly air sensitive.

Complex 1 has been characterized spectroscopically and by a single-crystal X-ray diffraction study (Figure 1). Its ^1H NMR spectrum shows a singlet at δ 5.87 due to the benzyl protons and two MeCp methyl resonances at δ 2.59 and 2.27 along with resonances due to the MeCp ring protons and the phenyl protons in the usual regions. The

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[5] For examples see: (a) Burgess, K.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1982**, 2085–2092. (b) Dekker, M.; Knox, G. R. *J. Chem. Soc., Chem. Commun.* **1967**, 1243–1244. (c) McGlinchey, M. J.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1970**, 1265.

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Table I. Crystal, Data Collection, and Refinement Parameters for $Mn_2C_{23}H_{21}N_3O_4$

	(a) Crystal Parameters		
fw	513.24	V, Å^3	2175.4 (3)
cryst system	monoclinic	Z	4
space group	$P2_1/n$	μ, cm^{-1}	11.49
a, Å	7.2175 (8)	ρ, g cm^{-3} (calcd)	1.567
b, Å	14.3614 (17)	size, mm	0.18 × 0.22 × 0.3
c, Å	21.2811 (20)	color	red-brown
β, deg	99.531 (9)		
	(b) Data Collection		
diffractometer	Nicolet R3	scan spd, deg min^{-1}	variable, 4–20
radiation	Mo Kα (λ = 0.71073 Å)		
monochromator	grphite	temp, °C	23
scan range, deg	$4 \le 2\theta \le 48$	std rflns	3 std/97 rflns
scan type	Ω	decay	none obsd
	(c) Data Reduction and Refinement		
rflns collected	3695	R_F,^{a} %	4.49
unique rflns	3421	R_{wF},^{a} % (g = 0.001)	4.76
unique rflns with $F_o \ge 3\sigma(F_o)$	2826	GOF	1.299
		Δ/σ (last cycle)	0.053
R(int), %	2.70	highest peak final diff Fourier, e Å^{-3}	0.41, 0.98 Å from Mn2
refined variable	290		
g	0.0008		

[a] $w^{-1} = \sigma^2(F_o) + g(F_o^2)$; $R_f = \sum|\Delta|/\sum|F_o|$; $R_{wf} = \sum(|\Delta|w^{1/2})/\sum(|F_o|w^{1/2})$; $\Delta = |F_o| - |F_c|$.

Table II. Atom Coordinates ($\times 10^4$) and Temperature Factors (Å^2 × 10^3)

atom	x	y	z	U_{iso}^{a}
Mn(1)	5427 (1)	5637 (1)	2683 (1)	29 (1)
Mn(2)	7004 (1)	4491 (1)	3680 (1)	29 (1)
N(1)	5166 (4)	5439 (2)	3536 (2)	30 (1)
N(2)	4379 (5)	5962 (2)	3882 (2)	38 (1)
N(3)	3561 (5)	6709 (2)	3517 (2)	40 (1)
O(1)	3558 (5)	7487 (2)	2591 (1)	54 (1)
O(2)	8570 (5)	6955 (2)	2802 (2)	61 (1)
O(3)	9589 (5)	4624 (3)	2749 (2)	64 (1)
O(4)	9582 (5)	5792 (3)	4443 (2)	69 (1)
C(1)	4042 (6)	6786 (3)	2902 (2)	37 (1)
C(2)	7350 (6)	6422 (3)	2771 (2)	37 (1)
C(3)	8434 (6)	4646 (3)	3059 (2)	44 (2)
C(4)	8548 (6)	5277 (3)	4145 (2)	43 (2)
C(5)	3005 (7)	7482 (3)	3884 (2)	49 (2)
C(6)	4639 (7)	7955 (3)	4305 (2)	44 (2)
C(7)	6462 (8)	7889 (4)	4181 (3)	65 (2)
C(8)	7937 (8)	8322 (4)	4572 (3)	74 (2)
C(9)	7614 (10)	8814 (4)	5085 (3)	75 (2)
C(10)	5837 (10)	8871 (5)	5227 (3)	85 (3)
C(11)	4371 (9)	8435 (4)	4839 (3)	68 (2)
C(12)	5190 (6)	4468 (3)	2007 (2)	41 (2)
C(13)	3437 (6)	4615 (3)	2201 (2)	39 (1)
C(14)	2861 (6)	5528 (3)	2028 (2)	42 (2)
C(15)	4266 (6)	5945 (3)	1726 (2)	41 (1)
C(16)	5710 (6)	5283 (3)	1704 (2)	39 (1)
C(17)	7412 (7)	5421 (4)	1378 (2)	57 (2)
C(18)	5551 (6)	3157 (3)	3461 (2)	43 (2)
C(19)	7498 (6)	3039 (3)	3604 (2)	45 (2)
C(20)	8124 (6)	3338 (3)	4235 (2)	42 (2)
C(21)	6531 (6)	3669 (3)	4478 (2)	40 (1)
C(22)	4937 (6)	3546 (3)	3996 (2)	42 (2)
C(23)	2949 (7)	3745 (4)	4067 (3)	67 (2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Selected Bond Distances and Angles for $Mn_2C_{23}H_{21}N_3O_4$

	(a) Bond Distances (Å)		
Mn(1)–Mn(2)	2.777 (1)	N(1)–N(2)	1.253 (5)
Mn(1)–N(1)	1.877 (3)	N(2)–N(3)	1.396 (5)
Mn(2)–N(1)	1.890 (3)	N(3)–C(1)	1.413 (6)
Mn(1)–CNT1^a	1.799 (3)	C(1)–O(1)	1.223 (5)
Mn(2)–CNT2^a	1.792 (3)	C(2)–O(2)	1.161 (5)
Mn(1)–C(2)	1.774 (4)	C(3)–O(3)	1.147 (6)
Mn(2)–C(3)	1.820 (5)	C(4)–O(4)	1.162 (5)
Mn(2)–C(4)	1.769 (4)	N(3)–C(5)	1.452 (6)
Mn(1)–C(1)	2.023 (4)	Mn(1)–C(3)	2.608 (5)
	(b) Bond Angles (deg)		
Mn(1)–Mn(2)–CNT2^a	121.6 (1)	N(1)–Mn(2)–C(4)	89.5 (2)
Mn(1)–Mn(2)–N(1)	42.3 (1)	C(3)–Mn(2)–C(4)	87.0 (2)
Mn(1)–Mn(2)–C(3)	65.3 (1)	Mn(1)–N(1)–Mn(2)	95.0 (2)
Mn(1)–Mn(2)–C(4)	100.9 (1)	Mn(1)–N(1)–N(2)	127.3 (3)
Mn(2)–Mn(1)–CNT1^a	121.6 (2)	Mn(2)–N(1)–N(2)	135.3 (3)
Mn(2)–Mn(1)–N(1)	42.7 (1)	N(1)–N(2)–N(3)	108.9 (3)
Mn(2)–Mn(1)–C(1)	117.6 (1)	N(2)–N(3)–C(1)	115.4 (3)
Mn(2)–Mn(1)–C(2)	94.7 (1)	N(2)–N(3)–C(5)	114.7 (3)
CNT1–Mn(1)–N(1)^a	134.2 (2)	C(5)–N(3)–C(1)	124.8 (3)
CNT1–Mn(1)–C(1)^a	109.6 (2)	N(3)–C(1)–O(1)	118.2 (4)
CNT1–Mn(1)–C(2)^a	124.4 (2)	Mn(1)–C(1)–N(3)	110.9 (3)
N(1)–Mn(1)–C(1)	76.6 (2)	Mn(1)–C(1)–O(1)	130.9 (3)
N(1)–Mn(1)–C(2)	101.3 (2)	Mn(1)–C(2)–O(2)	176.8 (3)
C(1)–Mn(1)–C(2)	82.2 (2)	Mn(2)–C(3)–O(3)	165.6 (4)
CNT2–Mn(2)–N(1)^a	123.0 (3)	Mn(2)–C(4)–O(4)	178.8 (4)
CNT2–Mn(2)–C(3)^a	120.8 (2)	Mn(1)–C(3)–O(3)	119.1 (4)
CNT2–Mn(2)–C(4)^a	122.5 (2)		
N(1)–Mn(2)–C(3)	105.1 (2)		
	(c) Dihedral Angle (deg)		
[Mn(1)–Mn(2)–N(1)]–[Mn(1)–C(1)–N(3)–N(2)–N(1)]^b			14.4 (3)

[a] CNT1 and CNT2 are the centers of the MeC_5H_4 rings, respectively, bonded to Mn(1) and Mn(2). [b] Deviations of atoms from best fit plane: Mn(1), −0.0232; N(1), 0.0010; N(2), 0.0331; N(3), −0.0621; C(1), 0.0493 Å.

IR spectrum in THF shows absorbances due to the carbonyl ligands at 1970, 1925, and 1885 cm^{-1} and the acyl group at 1626 cm^{-1}. A parent ion at m/z 513 is apparent in the mass spectrum of 1.

Structural Characterization of Complex 1. An Ortep drawing of complex 1 is shown in Figure 1, and the important structural parameters are given in Tables I–III. The molecule consists of two manganese atoms bridged by one nitrogen of the μ-C(O)N(CH_2Ph)N_2 ligand. One Mn is further coordinated by a η^5-$CH_3C_5H_4$ ligand and two CO's while the other Mn is coordinated by a η^5-$CH_3C_5H_4$ ligand, one CO, and the acyl carbon of the μ-C(O)N(CH_2Ph)N_2 ligand. An additional carbonyl, C(3)–O(3), appears to be weakly semibridging between the two Mn atoms as indicated by its Mn(2)–C(3)–O(3) angle of 165.6 (4)° and the Mn(1)–C(3) distance of 2.608 (5) Å.[10] The

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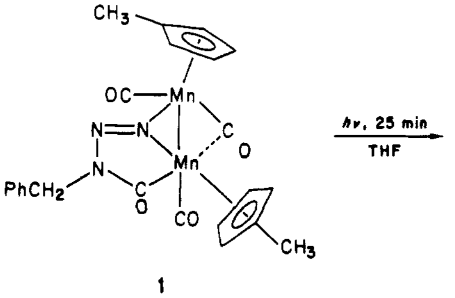
(10) See references in: Colton, R.; McCormick, M. J. *Coord. Chem. Rev.* **1980**, *31*, 1–52.

Mn–Mn distance of 2.777 (1) Å is well within the range of Mn–Mn single bonds as reviewed by Bernal, Creswick, and Herrmann.[11]

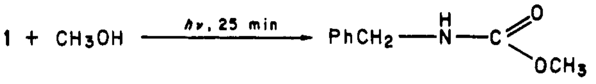
The structural parameters for the $\mu\text{-}C(O)N(R)N_2$ ligand in complex 1 compare well with those determined for the previously characterized complexes with similar ligands. The bond lengths within the C–N–N–N ring of this ligand in complex 1 are 1.413 (6), 1.396 (5), and 1.253 (5) Å, respectively, compared to 1.385 (16), 1.414 (12), and 1.260 (11) Å for $(C_5Me_5)_2Mo_2(NEt)(CO)_2[\mu\text{-}C(O)N(Et)N_2]$[9b] and 1.42 (2), 1.38 (2), and 1.24 (2) Å for $Os_3(CO)_{10}(NCMe)[\mu\text{-}C(O)N(Ph)N_2]$.[9a] Note that these distances indicate that N(2)–N(3) is a single bond while N(1)–N(2) has predominantly double-bond character as illustrated in the above drawing of 1. The bridging nitrogen atom symmetrically bridges the two metal atoms as indicated by the similar Mn(1)–N(1) and Mn(2)–N(1) distances of 1.877 (3) and 1.890 (3) Å.

Formation of Benzyl Isocyanate upon Irradiation of 1. Irradiation of green THF solutions of 1 gives an orange solution after ca. 25 min during which time the IR absorbances due to 1 disappear and are replaced by bands at 2265, 1923, and 1848 cm^{-1}. The latter two bands are due to $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(THF)$ while the first is characteristic of benzyl isocyanate, indicating the reaction shown in eq 5. This reaction is not stoichiometric in carbon monoxide and the extra CO necessary to form $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(THF)$ must come from some decomposition of 1. Irradiation of 1 under a CO atmosphere gives $PhCH_2NCO$ and a mixture of $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3$ and $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(THF)$, with the latter slowly converting into the former. Photolysis of 1 in methanol solution produces methyl *N*-benzylcarbamate, apparently formed by reaction of MeOH with the initially formed $PhCH_2NCO$ (eq 6). The organometallic products of this latter reaction were not identified.



1

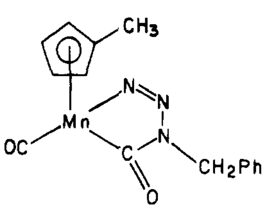
$$2(MeCp)Mn(CO)_2(THF) + PhCH_2NCO \quad (5)$$



$$1 + CH_3OH \xrightarrow{h\nu,\ 25\ min} PhCH_2\text{—}\overset{H}{N}\text{—}C(=O)OCH_3 \quad (6)$$

Discussion

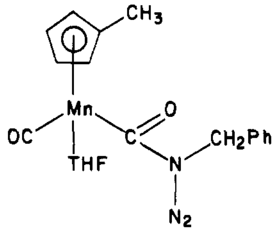
As mentioned in the Introduction, the reaction of organic azides with metal carbonyls to give isocyanates is a well-documented reaction. Although the reaction is believed to proceed via addition of the azide to a metal carbonyl carbon, to our knowledge no report of the characterization of a mononuclear complex containing the intact C(O)N(R)N_2 ligand which results from azide + CO coupling has appeared. Even though a mononuclear starting complex was used in this study, the product 1 was binuclear with a bridging $\mu\text{-}C(O)N(R)N_2$ ligand. Addition of benzyl azide to a carbonyl in $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(THF)$ followed by displacement of THF by the terminal nitrogen could lead to mononuclear 2 which may be an intermediate en route to 1, with 1 formed by displacement of THF from a second molecule of $(MeCp)Mn(CO)_2(THF)$ by the basic α-nitrogen of 2.



2

An interesting aspect of the synthesis of 1 is its formation only during the concentration of THF solutions of $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(THF)$ and benzyl azide. We suspect this is due to an unfavorable equilibrium involving addition of $PhCH_2N_3$ to $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(THF)$ (eq 7) which must lie in the direction of the reactants since in dilute THF solution there is no spectroscopic evidence for any interaction between these two molecules. Only during concentration of the solution is product formation observed which is presumably a consequence of the increased probability of capture of 3, or 2 which would derive from 3, by $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(THF)$. Alternatively, the experimental observations may reflect an unfavorable equilibrium in which $PhCH_2N_3$ must displace a coordinated THF in $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(THF)$ before reaction can proceed, and this equilibrium shifts to the right as the THF concentration decreases.

$$(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(THF) + PhCH_2N_3 \rightleftharpoons$$



(7)

3

The photoconversion of 1 into $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(THF)$ and $PhCH_2NCO$ completes a cycle in which the net result is carbonylation of benzyl azide via 1. This is a unique example of a reaction sequence which proceeds from a mononuclear complex to a binuclear species and then back to the mononuclear complex, where the binuclear species is a necessary component for stabilizing a reactive intermediate so that it can be subsequently transformed.

Experimental Section

$(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3$ (Pressure Chemical Co.), benzyl azide, and benzyl isocyanate (Alfa) were purchased from commercial sources and used as received. Solvents used were dried and degassed by standard methods. All manipulations, unless otherwise specified, were conducted under prepurified N_2 using standard Schlenk and high vacuum line techniques. Instruments used in this research were as previously described.[12] Field desorption mass spectra were obtained by Guy Steinmetz and R. J. Hale at the Tennessee Eastman Co., Kingsport, TN. Electron-impact mass spectra were obtained by using an AEI-MS9 mass spectrometer with a source voltage of 70 eV and probe temperatures in the 50–200 °C range. Photolyses were conducted in Pyrex Schlenk vessels using an unfiltered Hanovia 450-W medium-pressure Hg discharge lamp. Elemental analyses were

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[11] Bernal, I.; Creswick, M.; Herrmann, W. A. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 1345–1346.

[12] Morrison, E. D.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 3541–3545.

performed by Schwartzkopf Microanalytical Laboratory, Woodside, NY.

Synthesis of (η^5-$CH_3C_5H_4)_2Mn_2(CO)_3[\mu$-$C(O)N(CH_2Ph)N_2]$ (1). Irradiation of a THF (70-mL) solution of (η^5-$CH_3C_5H_4$)$Mn(CO)_3$ (0.300 mL, 1.918 mmol) at 0–5 °C under flowing N_2 for 1.5 h gave a purple solution of (η^5-$CH_3C_5H_4$)$Mn(CO)_2$(THF). Photolysis was ceased, and benzyl azide (0.765 g, 5.754 mmol) was added to the cold solution via syringe. Solvent was removed under vacuum at 0 °C leaving a dark green residue which was stored at 0 °C overnight. Chromatography on SiO_2 using CH_2Cl_2 as eluent yielded first a light yellow band containing (η^5-$CH_3C_5H_4$)$Mn(CO)_3$ and benzyl azide and a second green band which gave 1 as a green solid upon solvent evaporation. Recrystallization from Et_2O gave red needles of 1 (0.085 g, 17% based on (MeCp)$Mn(CO)_3$). Anal. Calcd for $C_{23}H_{21}Mn_2N_3O_4$: C, 53.80; H, 4.09. Found: C, 53.67; H, 4.27. IR: ν_{CO} (THF) 1970 (vs), 1925 (s), 1885 (m), 1626 (m) cm^{-1}. MS: *m/z* 513 (M^+). ^{1}H NMR (CD_2Cl_2): δ 7.81–7.71 (m, Ph), 5.87 (s, CH_2), 5.28–4.76 (m, br, Cp), 2.59 (s, br, CH_3), 2.27 (s, br, CH_3).

Irradiation of 1 in THF Solution. A THF (15-mL) solution of 1 (0.030 g, 0.058 mmol) was irradiated for 25 min during which time the color of the solution changed from green to orange. The infrared spectrum showed that bands attributable to 1 were replaced by bands at 2265 (w) cm^{-1} due to $PhCH_2NCO$ and at 1923 (s) and 1848 (s) cm^{-1} for (η^5-$CH_3C_5H_4$)$Mn(CO)_2$(THF).

Irradiation of 1 in MeOH Solution. A methanol solution of 1 (0.030 g, 0.058 mmol) was irradiated for 25 min, during which time the color changed from green to orange. The solution was then warmed to 60 °C for 30 min. Solvent was removed on a rotary evaporator in air, and extraction with $CHCl_3$ (3 × 10 mL) gave a clear solution which was filtered and placed in a 50-mL Schlenk flask. The solvent was evaporated, and the flask was fitted with a cold finger (5–10 °C). Sublimation at 22 °C and 0.001 mmHg gave methyl *N*-benzylcarbamate (0.006 g, 0.036 mmol) as a white crystalline solid in 67% yield based on 1. IR ($CHCl_3$): 3440 (w) (ν(NH)), 1719 (s), 1689 (s) (ν(CO)) cm^{-1}. MS: *m/z* 165 (M^+) + expected fragments; *m/z* calcd for $C_9H_{11}NO_2$ 165.0790, found 165.0798. ^{1}H NMR (Me_2SO-d_6): δ 8.51 (t, br, J = 6.3 Hz, NH_a), 7.71 (t, br, J = 6.2 Hz, NH_b), 7.34–7.24 (m, Ph_a + Ph_b), 4.28 (d, J = 6.3 Hz, CH_{2a}), 4.15 (d, J = 6.2 Hz, CH_{2b}), 3.53 (s, OCH_{3a}), 3.35 (s, OCH_{3b}). Methyl *N*-benzylcarbamate exists in Me_2SO solution as two isomers related by a rotation around the C–N bond, labeled here as a and b (a:b = 1:2.7).

X-ray Structure of 1. A suitable crystal of 1 was obtained by recrystallization from diethyl ether. It was encapsulated in epoxy cement on a fine glass fiber and mounted on an eucentric goniometer. Unit-cell dimensions were obtained from the angular settings of 25 reflections, 22° ≤ 2θ ≤ 30°, and systematic absences uniquely defined the centrosymmetric monoclinic space group $P2_1/n$. Details of data collection, reduction, and refinement are listed in Table I.

No correction for absorption was applied to the intensity data (relative transmission, 1:1.17). The two Mn atoms were located by direct methods (Solv) and directly provided the remaining non-hydrogen atoms from a subsequent difference Fourier synthesis. All non-hydrogen atoms were refined with anisotropic temperature factors. Hydrogen atoms were assigned idealized, updated locations (d(C–H) = 0.95 Å; $U = 1.2\ U_{iso}$ attached atom) but not refined. The correct ring methyl group rotational orientations were determined by locating one or more hydrogen atoms on each. Computer programs are those contained in the P3 and Shelxtl (version 4.1) libraries distributed by the Nicolet Corp. The slope of a normal probability plot was 1.105, attesting to the accuracy of the weighting scheme.

Atomic coordinates for the non-hydrogen atoms are provided in Table II, and selected bond distances and angles are given in Table III. Complete lists of bond distances and angles, anisotropic temperature factors, hydrogen atom coordinates, and observed vs. calculated structure factors are available as supplementary material.

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Registry No. 1, 100993-23-5; (η^5-$CH_3C_5H_4$)$Mn(CO)_3$, 12108-13-3; (η^5-$CH_3C_5H_4$)$Mn(CO)_2$(THF), 51922-84-0; $PhCH_2NCO$, 3173-56-6; benzyl azide, 622-79-7; methyl *N*-benzylcarbamate, 5817-70-9.

Supplementary Material Available: Tables of anisotropic temperature factors and structure factors and complete lists of bond lengths and angles and hydrogen atom coordinates for 1 (22 pages). Ordering information is given on any current masthead page.