Reactions of Isocyanide-Substituted Dimanganese Carbonyl Complexes with Alkynes. Alkyne-Isocyanide Coupling and the Synthesis of Metalated N-Substituted **Pyridines**

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Received September 7, 1994[®]

When activated by Me_3NO in the presence of MeCN, the compounds $Mn_2(CO)_9(CNR)$ (1a,b; R = Me, Ph) react with MeO₂CC=CCO₂Me to yield the new compounds Mn₂(CO)₈[μ - $(MeO_2C)C=C(CO_2Me)C=NR$] (2a,b; R = Me, Ph) in yields of 40% and 32%, respectively. Minor products, $Mn_2(CO)_7(CNR)[\mu-(MeO_2C)C=C(CO_2Me)C=O]$ (3a,b; R = Me, Ph) were also formed. Compound 2a was characterized crystallographically. The structure shows that the isocyanide ligand was coupled to the alkyne, and the nitrogen atom is coordinated to one of the manganese atoms to form a five-membered cyclo-mangana enimine ring. One of the carboxylate groups is coordinated to the other manganese atom. The compounds $Mn_{2}(CO)_{7}[\mu-\eta^{4}-\dot{C}N(Me)CHCHC(CO_{2}Me)\dot{C}(CO_{2}Me)] (4a), Mn_{2}(CO)_{7}[\mu-\eta^{4}-\dot{C}N(Ph)CHCHC(CO_{2}-\mu)\dot{C}(CO_{2}Me)] (4a), Mn_{2}(CO)_{7}[\mu-\eta^{4}-\dot{C}N(Ph)CHCHC(CO_{2}-\mu)\dot{C}$

Me) $\overset{\downarrow}{C}(CO_2Me)$] (4b), and Mn₂(CO)₇[μ - η ⁴- $\overset{\downarrow}{C}N(Me)CHC(CO_2Me)C(CO_2Me)\overset{\downarrow}{C}(CO_2Me)$] (4c) were prepared in yields of 27%, 32%, and 31%, respectively, by treatment of 2a,b with C_2H_2 and of 2a with $HC_2(CO_2Me)$ in the presence of UV irradiation. Compound 4a was characterized crystallographically. This compound contains a metalated N-methylpyridine ring formed by a 1,4-cycloaddition of the alkyne to the enimine grouping in compound 2a. One of the metal atoms was shifted to a π -bonding coordination involving four of the carbon atoms of the pyridine ring. Crystal data: for **2a** space group $P2_1/n$, a = 10.981(4) Å, b = 11.425(2) Å, c = 16.780(5) Å, $\beta = 92.00(3)^\circ$, Z = 4, 1526 reflections, R = 0.041; for 4a space group $P2_1/n$, a = 9.655(2) Å, b = 17.538(5) Å, c = 12.599(1) Å, $\beta = 107.03(1)^{\circ}$, Z = 4, 1950 reflections, R = 0.033.

Introduction

Metal-assisted coupling reactions between alkynes and CO have provided routes for the synthesis of a wide variety of new organic ligands1 and new organic molecules.² Recent studies have shown that ligands formed by the coupling of alkynes to CO in the presence of dinuclear manganese carbonyl complexes frequently results in the formation of groupings in which the oxygen atom of the CO group is coordinated to one or both of the metal atoms. $^{3-6}$ This coordination can have a significant effect upon the subsequent reactivity of the

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complex and the ligand grouping itself.⁷ For example, we have recently shown that the metalated enone complex $Mn_2(CO)_8[\mu-(EtO_2C)C=C(CO_2Et)C=O]$ (A) will decarbonylate and add an alkyne in the presence of UV irradiation to yield complexes containing metalated

pyran rings (e.g. $Mn_2(CO)_7[\mu-\eta^4-COCR^2CR^1C(CO_2Et)C (CO_2Et)$] (B)) by a 1,4-cycloaddition of alkynes to the enone grouping in A (eq 1).



Studies of the coupling of alkynes to isocyanides have been far fewer.⁸ We have now found that the compounds $Mn_2(CO)_9(CNR)$ (1a,b; R = Me, Ph) can be activated by treatment with Me₃NO in the presence of NCMe toward reaction with $MeO_2CC \equiv CCO_2Me$. The principal products 2 obtained from these reactions contain cyclometalated enimine groupings formed by the

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coupling of the alkyne to the isocyanide ligand and the coordination of the nitrogen atom to one of the manganese atoms.



Like compound A, these compounds also add a second alkyne in the presence of UV irradiation. These products contain metalated N-substituted pyridine ligands formed by a 1,4-cycloaddition of the alkyne to the enimine grouping in the compounds 2. The results of this study are reported here.

Experimental Section

Unless otherwise indicated, all reactions were carried out under an atmosphere of nitrogen. Hexane was freshly distilled over Na prior to use. MeCN and CH₂Cl₂ solvents were dried over CaH₂. HC=CH was purchased from Union Carbide Inc.; HC≡CCO₂Me (99%) and MeO₂CC≡CCO₂Me (99%) were purchased from Aldrich Co. and were used without further purification. Trimethylamine N-oxide dihydrate was dehydrated by using a Dean-Stark apparatus with benzene as the solvent prior to use. CNMe,9 CNPh,9 and Mn₂(CO)9(NCMe)¹⁰ were prepared by the reported procedures. UV irradiations were performed on solutions in Pyrex glassware by using an externally positioned 1000-W high-pressure mercury lamp purchased from Cooper Lighting, Vicksburg, MS. TLC separations were performed in air using silica gel (60 Å, F_{254}) on plates (Whatman, 0.25 mm). IR spectra were recorded on a Nicolet 5DXB FT-IR spectrophotometer. ¹H NMR spectra were taken at 400 MHz on a Bruker Am-400 spectrometer. Elemental analyses were performed by Oneida Research Serivces Inc., Whitesboro, NY.

Preparation of Mn₂(CO)₉(CNMe) (1a) and Mn₂(CO)₉-(CNPh) (1b). (a) Mn₂(CO)₉(CNMe). A solution of a 250.0mg amount (0.62 mmol) of $Mn_2(CO)_9(NCMe)$ and 38.9 μL (0.74 mmol) of CNMe in 200 mL of CH₂Cl₂ was heated to reflux for 2 h. After the mixture was cooled to room temperature, the solvent was removed in vacuo, and the residue was isolated by column chromatography. Elution with a hexane/ CH_2Cl_2 (5/ 1) solvent mixture yielded 218.0 mg of yellow Mn₂(CO)₉(CNMe) (1a; 87%). It was spectroscopically identical in the IR to the compound with the same formula reportedly obtained from the reaction of Mn₂(CO)₁₀ with CNMe.¹¹

(b) $Mn_2(CO)_{\theta}(CNPh)$. By a procedure similar to that described above, Mn₂(CO)₉(CNPh) was prepared in 88% yield from the reaction of Mn₂(CO)₉(NCMe) and CNPh. It was spectroscopically identical to the material with the same formula reportedly obtained from the reaction of MeMn(CO)5 with CNPh.¹²

Reaction of 1a with MeO₂CC=CCO₂Me. A 300.0-mg amount (0.74 mmol) of 1a and a 67.3-mg amount (0.90 mmol) of Me₃NO in 50 mL of MeCN was stirred at 25 °C for 30 min. The solvent was removed under vacuum, and the orange solid was redissolved in 50 mL of CH₂Cl₂. To this solution was added a 138.5- μ L amount (1.12 mmol) of MeO₂CC=CCO₂Me via a syringe. This solution was then stirred at 25 °C for 20 h. The solvent was removed by rotary evaporation, and the product was isolated by chromatography over a silica gel column. This yielded 16.2 mg of unreacted 1a (eluted with a hexane/CH₂Cl₂ (4/1) solvent mixture) 155.1 mg of yellow Mn₂(CO)₈[µ-(MeO₂C)C=C(CO₂Me)C=NMe] (2a; 40% yield (eluted with a hexane/CH₂Cl₂ (2/1) solvent mixture)) and 45.8 mg of orange $Mn(CO)_4[\mu-(MeO_2C)C=C(CO_2Me)C=O)]Mn(CO)_3$ -(CNMe) (3a; 12% yield (eluted by a hexane/CH₂Cl₂ (1/1) solvent mixture)). Spectral data for 2a: IR (ν_{CO} in hexane, cm⁻¹) 2095 (w), 2080 (m), 2015 (vs), 1999 (s), 1960 (s), 1951 (m), 1724 (w, br), 1600 (w, br), 1548 (w, br); ¹H NMR (δ in CDCl₃, ppm) 3.87 (s, 3H, OCH₃), 3.83 (s, 3H, OCH₃), 3.78 (s, 3H, NCH₃). Anal. Calcd (found): C, 37.20 (37.05); H, 1.75 (1.41); N, 2.70 (2.69). Spectral data for **3a**: IR ($\nu_{CO,CN}$ in hexane, cm⁻¹) 2191 (w, br), 2090 (m), 2035 (vs), 2025 (s), 2014 (s), 2004 (s), 1976 (s), 1959 (s), 1918 (s), 1947 (s), 1724 (w, br), 1609 (m, br), 1542 (w, br); ¹H NMR (δ in CDCl₃, ppm) 3.89 (s, 3H, OCH₃), 3.84 (s, 3H, OCH₃), 3.35 (s, 3H, NCH₃). Anal. Calcd (found): C, 37.20 (36.19); H, 1.75 (1.77); N, 2.70 (2.78).

Reaction of 1b with MeO₂CC≡CCO₂Me. Using a procedure similar to that described above, a reaction of 370.0 mg (0.796 mmol) of 1b with 1.5 equiv of MeO₂CC=CCO₂Me yielded two new compounds: Mn₂(CO)₈[(MeO₂C)C=C(CO₂-Me)C=NPh] (2b; 32% yield) and Mn(CO)₄[(MeO₂C)C=C(CO₂-MeC=O)]Mn(CO)₃(CNPh) (3b; 2% yield). Spectral data for **2b**: IR (ν_{C0} in hexane, cm⁻¹) 2003 (s), 2079 (m), 2011 (vs), 2005 (vs), 1996 (m), 1968 (s), 1723 (w, br), 1600 (w, br), 1541 (w, br); ¹H NMR (δ in CDCl₃, ppm) 7.39-7.03 (m, 5H, Ph), 3.90 (s, 3H, OCH₃), 3.86 (s, 3H, OCH₃). Spectral data for 3b: IR $(\nu_{\rm CO,CN} \text{ in hexane, cm}^{-1})$ 2143 (w, br), 2090 (m), 2031 (vs), 2015 (s), 2006 (s), 1981 (s), 1960 (s), 1952 (s), 1724 (w, br), 1608 (m, br), 1524 (w, br); ¹H NMR (δ in CDCl₃, ppm) 7.38 (m, 5H, Ph), 3.90 (s, 3H, OCH₃), 3.87 (s, 3H, OCH₃).

Reaction of the Compounds 2 with Alkynes. (a) 2a with HC=CH. A 50.0-mg (0.097-mmol) amount of 2a was dissolved in 300 mL of hexane in a 500-mL Pyrex flask. The solution was purged with HC=CH for 15 min and then exposed to UV light at 25 °C for 5 min. The solvent was then removed under vacuum, and the residue was separated by TLC using a hexane/CH₂Cl₂ (1/1) solvent mixture. This yielded 2.2 mg

 $\dot{C}N(Me)CHCHC(CO_2Me)\dot{C}(CO_2Me)]$ (4a) in 27% yield. Spectra data for 4a: IR (v_{CO} in hexane, cm⁻¹) 2100 (w), 2021 (s), 2008 (m), 1953 (m), 1935 (m), 1921 (m), 1730 (w, br), 1577 (w, br); ¹H NMR (δ in CDCl₃, ppm) 6.05 (d, ³J_{H-H} = 4.7 Hz, 1H, CH), 4.16 (d, ${}^{3}J_{H-H} = 4.7$ Hz, 1H, CH), 3.88 (s, 3H, OCH₃), 3.73 (s, 3H, OCH₃), 3.32 (s, 3H, NCH₃). Anal. Calcd (found): C, 39.64 (39.34); H, 2.15 (2.15); N, 2.72 (2.76).

(b) 2b with HC=CH. Using a procedure similar to that described above, irradiation of a solution of 50.0 mg of 2b in hexane with HC=CH (slow purge) gave the compound

 $Mn_2(CO)_7[\mu-\eta^4-\dot{C}N(Ph)CHCHC(CO_2Me)\dot{C}(CO_2Me)]$ (4b) in 32% yield. Spectral data for 4b: IR (ν_{CO} in hexane, cm⁻¹) 2097 (w), 2016 (s), 2006 (m), 1968 (m), 1934 (m), 1921 (m), 1730 (w, br), 1577 (w, br); ¹H NMR (δ in CDCl₃, ppm) 7.51-6.93 (m, 5H, Ph), 6.13 (d, ${}^{3}J_{H-H} = 4.5$ Hz, 1H, CH), 4.43 (d, ${}^{3}J_{H-H} = 4.5$ Hz, 1H, CH), 3.93 (s, 3H, OCH₃), 3.76 (s, 3H, OCH₃).

(c) 2a with HC=CCO₂Me. A 20.0-mg amount (0.039)mmol) of 2a and a 17.4- μ L amount of HC=CCO₂Me were dissolved in 80 mL of hexane. The solution was exposed to UV light at 25 °C for 5 min. The solvent was then removed under vacuum, and the residue was separated by TLC using a bexane/CH₂Cl₂ (1/1) solvent mixture to give 0.8 mg of unreacted starting material and 6.9 mg of orange Mn₂-

 $(CO)_7[\mu - \eta^4 - \dot{C}N(Me)CHC(CO_2Me)C(CO_2Me)\dot{C}(CO_2Me)]$ (4c) in 31% yield. Spectral data for 4c: IR (ν_{CO} in hexane, cm⁻¹) 2101 (w), 2015 (s), 1958 (m), 1950 (m), 1934 (m), 1733 (w, br), 1716 (w, br), 1585 (w, br); ¹H NMR (δ in CDCl₃, ppm) 6.58 (s, 1H, CH), 3.89 (s, 3H, OCH₃), 3.76 (s, 6H, OCH₃), 3.44 (s, 3H, NCH_3).

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Table 1. Crystallographic Data for Compounds 2a and 4a

	2a	4 a
empirical formula	Mn ₂ O ₁₂ NC ₁₆ H ₉	Mn ₂ O ₁₁ NC ₁₇ H ₁₁
fw	517.12	515.15
cryst syst	monoclinic	monoclinic
lattice params		
a (Å)	10.981 (4)	9.655(2)
b (Å)	11.425(2)	17.538(5)
<i>c</i> (Å)	16.780(5)	12.599(1)
β (deg)	92.00(3)	107.03(1)
$V(Å^3)$	2103.9(9)	2039.9(6)
space group	$P2_1/n$ (No. 14)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)
Ζ	4	4
$D_{\text{calc}}, \text{g/cm}^3$	1.63	1.68
μ (Mo K α) (cm ⁻¹)	12.62	12.98
temp (°C)	20	20
$2\theta_{\max}$ (deg)	42.0	42.0
no. of obs rflns: total; $I > 3\sigma(I)$	2409; 1526	2291; 1950
no. of variables	280	276
residuals: ^{<i>a</i>} R ; R_w	0.041; 0.036	0.033; 0.040
goodness-of-fit indicator (GOF)	2.33	2.73
max shift in final cycle	0.00	0.06
largest peak in final diff map $(e/Å^3)$	0.26	0.33
abs cor: max/min		empirical, 1.0/0.92

 ${}^{a}R = \sum_{hkl} (||F_{o}| - |F_{c}|| \sum_{hkl} |F_{o}|; R_{w} = [\sum_{hkl} (|F_{o}| - |F_{c}|^{2}) \sum_{hkl} |F_{o}^{2}|^{1/2}, w$ = $1/\sigma^{2}(F_{o}); \text{ GOF} = [\sum_{hkl} (|F_{o}| - F_{c}|/\sigma(F_{o})] / (n_{\text{data}} - n_{\text{vari}}).$

Crystallographic Analysis. Crystals of compounds 2a and 4a suitable for X-ray diffraction analysis were grown by slow evaporation of solvent from a solution in a hexane/CH2- $Cl_2(1/1)$ solvent mixture at 25 °C. All crystals that were used in diffraction intensity measurements were mounted in thinwalled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer by using graphite-monochromated Mo Ka radiation. The unit cells were determined and refined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. All data processing was performed on a Digital Equipment Corp. VAXstation 3520 computer by using the TEXSAN motif structure solving program library obtained from Molecular Structure Corp., The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures.^{13a} Anomalous dispersion corrections were applied to all non-hydrogen atoms.^{13b} Lorentz/ polarization (Lp) corrections were applied to the data for each structure. Full-matrix least-squares refinements minimized the function $\sum_{hkl} w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F_o)^2$, $\sigma(F_o) = \sigma$ - $(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{\rm raw})^2 + (0.02I_{\rm net})^2]^{1/2}/Lp$. Both structures were solved by a combination of direct methods (MITH-RIL) and difference Fourier syntheses. Crystal data and results of the analyses are listed in Table 1.

Both compounds crystallized in the monoclinic crystal system in the space group $P2_1/n$ which was identified uniquely from the patterns of systematic absences observed in the data. For both structures least-squares refinements were completed using anisotropic thermal parameters for all non-hydrogen atoms. The positions of all hydrogen atoms were calculated by assuming idealized geometries with C-H = 0.95 Å. The scattering contributions of calculated hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Results

When they are treated with Me₃NO in the presence of NCMe, the compounds $Mn_2(CO)_9(CNR)$ (1a,b; R = Me, Ph) can be activated toward a subsequent reaction with the alkyne MeO₂CC=CCO₂Me. The principal products obtained from this sequence of reactions are



Figure 1. ORTEP diagram of $Mn_2(CO)_8[\mu-(MeO_2C)C=C-(CO_2Me)C=NMe]$ (2a) showing 50% probability thermal ellipsoids.

Table 2. Positional Parameters and B(eq) Values for 2a

atom	x	у	z	$B(eq), Å^2$
Mn(1)	0.26983(12)	0.15771(11)	0.88986(08)	3.87(6)
Mn(2)	-0.16542(11)	0.25184(11)	0.83054(07)	3.65(6)
O(1)	0.2869(05)	0.4446(06)	1.0021(04)	6.4(4)
O(2)	0.3240(05)	0.4790(05)	0.8725(03)	4.7(3)
O(3)	0.0486(04)	0.5321(05)	0.8968(03)	4.3(3)
O(4)	-0.1049(05)	0.4201(04)	0.8553(03)	4.2(3)
O (11)	0.5134(06)	0.2155(06)	0.9604(04)	8.0(5)
O(12)	0.3601(06)	-0.0834(06)	0.8573(05)	9.4(5)
O(13)	0.1750(06)	0.1094(06)	1.0502(04)	7.8(4)
O(14)	0.3313(06)	0.2353(06)	0.7267(04)	7.1(4)
O(21)	-0.2755(06)	0.0222(05)	0.7988(04)	7.2(4)
O(22)	-0.1854(06)	0.1944(06)	1.0020(04)	7.3(4)
O(23)	-0.1107(06)	0.2701(06)	0.6576(04)	6.7(4)
O(24)	-0.4166(05)	0.3505(6)	0.8088(04)	8.0(4)
N(1)	0.0918(05)	0.1321(05)	0.8493(04)	3.8(4)
C(1)	0.0011(08)	0.4308(07)	0.8760(05)	3.8(5)
C(2)	0.0802(07)	0.3279(07)	0.8782(04)	3.1(4)
C(3)	0.1972(07)	0.3208(06)	0.9013(04)	3.2(4)
C(4)	0.2708(07)	0.4228(07)	0.9342(06)	4.1(5)
C(5)	0.0166(07)	0.2190(07)	0.8515(04)	3.3(4)
C(6)	0.0504(07)	0.0146(07)	0.8251(05)	5.1(5)
C (7)	-0.0350(07)	0.6306(07)	0.8945(05)	4.9(5)
C(8)	0.4024(08)	0.5766(08)	0.8980(06)	7.3(6)
C(11)	0.4201(09)	0.1944(08)	0.9333(05)	5.5(5)
C(12)	0.3229(08)	0.0059(08)	0.8706(06)	6.0(6)
C(13)	0.2135(08)	0.1250(07)	0.9896(06)	4.9(5)
C(14)	0.3100(07)	0.2046(07)	0.7891(06)	4.6(5)
C(21)	-0.2296(07)	0.1098(08)	0.8094(06)	5.2(5)
C(22)	-0.1810(07)	0.2199(07)	0.9368(06)	4.5(5)
C(23)	-0.1303(08)	0.2673(07)	0.7237(06)	4.4(5)
C(24)	-0.3207(08)	0.3143(07)	0.8177(06)	5.1(5)

the new compounds $Mn_2(CO)_8[\mu-(MeO_2C)C=C(CO_2-Me)C=NR]$ (**2a,b**; R = Me, Ph) obtained in the yields of 40% and 32%, respectively. An accompanying minor product formulated as $Mn_2(CO)_7(CNR)[\mu-(MeO_2C)-C=C(CO_2Me)C=O]$ (**3a,b**; R = Me, Ph) was also obtained in each respective reaction. Compound **2a** was characterized structurally by a single-crystal X-ray diffraction analysis, and an ORTEP drawing of its molecular structure is shown in Figure 1. Final atomic positional parameters are listed in Table 2. Selected interatomic distances and angles are given in Tables 3 and 4, respectively. The molecule contains a enimine grouping that was formed by the coupling of the isocyanide ligand to the alkyne. Formally, this group has been inserted into the metal-metal bond that exists

^{(13) (}a) International Tables for X-ray Crystallography; Kynoch Press: Birmingham, England, 1975; Vol. IV, Table 2.2B, pp 99-101.
(b) Ibid., Table 2.3.1, pp 149-150.

Table 3. Intramolecular Distances for 2a^a

Mn(1) - N(1)	2.069(6)	O(2)-C(4)	1.367(9)
Mn(1) - C(3)	2.039(7)	O(2)-C(8)	1.463(9)
Mn(1) - C(11)	1.83(1)	O(3) - C(1)	1.311(8)
Mn(1) - C(12)	1.86(1)	O(3) - C(7)	1.452(8)
Mn(1) - C(13)	1.84(1)	O(4) - C(1)	1.209(8)
Mn(1) - C(14)	1.84(1)	O-C (av)	1.130(9)
Mn(2) - O(4)	2.071(5)	N(1) - C(5)	1.293(8)
Mn(2) - C(5)	2.052(8)	N(1) - C(6)	1.470(8)
Mn(2) - C(21)	1.799(9)	C(1) - C(2)	1.46(1)
Mn(2) - C(22)	1.83(1)	C(2) - C(3)	1.331(9)
Mn(2) - C(23)	1.86(1)	C(2) - C(5)	1.49(1)
Mn(2) - C(24)	1.85(1)	C(3) - C(4)	1.51(1)
O(1)-C(4)	1.173(9)		

^a Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

in the dimanganese species 1a,b. The nitrogen atom N(1) is coordinated to the manganese atom Mn(1), and the carbon C(5) is coordinated to the metal atom Mn-(2). The Mn(1)-N(1) = 2.069(6) Å distance is slightly shorter than the corresponding distance of 2.078(3) Å found for the Mn-O distance in the metalated enone complex A shown in eq 1,⁷ while the Mn(2)-C(5)distance (2.052(8) Å) is slightly longer than that found in compound A(1.954(7) Å). Formally, there is a double bond between the atoms C(2) and C(3) and C(5) and N(1), and this is reflected in the short bond distances (1.331(9) and 1.293(8) Å). The C(2)-C(5) distance is formally single at 1.49(1) Å. One of the carboxylate groups is coordinated to the manganese atom Mn(2)(Mn(2)-O(4) = 2.071(5) Å), and this results in the formation of a second five-membered ring which is similar to that found in A. The IR spectrum of 2a shows two low-energy absorptions at 1600 and 1548 cm^{-1} , which can be attributed to the stretching frequencies of the C=O of the coordinated carboxylate and C=N of the imine groups, respectively. Compound 2b is believed to be structurally analogous to that of 2a.

The minor products 3a,b exhibit high-frequency absorptions at 2191 and 2143 cm⁻¹, respectively, that are characteristic of coordinated isocyanide ligands, which indicates that the isocyanide has not been coupled to the alkyne in the formation of these products. However, the presence of two low-energy absorptions (1609, 1542 cm⁻¹ for 3a and 1600, 1541 cm⁻¹ for 3b) indicates the formation of a molecule with a structure similar to that of A and 2a. Thus, these molecules are formulated as isocyanide-substituted derivatives of A. A variety of different isomers may exist depending upon which metal atom contains the isocyanide ligand



Possible isomers of 3a-b

and also at which site on a given metal atom the isocyanide ligand resides.

When the cyclometalated enimine complexes 2a,bwere irradiated in the presence of a slow purge with HC=CH, the new compounds $Mn_2(CO)_7[\mu-\eta^4-CN(Me)-CHCHC(CO_2Me)C(CO_2Me)]$ (4a) and $Mn_2(CO)_7[\mu-\eta^4-CN(Ph)CHCHC(CO_2Me)C(CO_2Me)]$ (4b) were obtained

Table 4. Intramolecular Bond Angles for 2a^a

		÷	
N(1)-Mn(1)-C(3)	78.0(3)	C(3)-C(2)-C(5)	118.4(7)
O(4) - Mn(2) - C(5)	80.3(3)	Mn(1) - C(3) - C(2)	113.9(6)
Mn(2) - O(4) - C(1)	116.8(5)	Mn(1) - C(3) - C(4)	122.2(6)
Mn(1) - N(1) - C(5)	118.6(5)	C(2) - C(3) - C(4)	123.9(7)
Mn(1) - N(1) - C(6)	120.0(5)	O(1) - C(4) - O(2)	125.5(8)
C(5) - N(1) - C(6)	121.2(6)	O(1) - C(4) - C(3)	125.4(8)
O(3) - C(1) - O(4)	122.4(8)	O(2) - C(4) - C(3)	108.9(7)
O(3) - C(1) - C(2)	118.2(7)	Mn(2) - C(5) - N(1)	139.0(6)
O(4) - C(1) - C(2)	119.4(8)	Mn(2) - C(5) - C(2)	110.1(5)
C(1)-C(2)-C(3)	128.5(7)	N(1) - C(5) - C(2)	110.9(6)
C(1) - C(2) - C(5)	113.1(7)	Mn-C-O (av)	177.0(9)

^a Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.



Figure 2. ORTEP diagram of $Mn_2(CO)_7[\mu-\eta^4-\dot{C}N(Me)-CHCHC(CO_2Me)C(CO_2Me)]$ (4a) showing 50% probability thermal ellipsoids.

in yields of 27% and 32%, respectively. Compound 4a was characterized structurally by a single-crystal X-ray diffraction analysis, and an ORTEP diagram of its molecular structure is shown in Figure 2. Final atomic positional parameters are listed in Table 5. Selected bond distances and angles are listed in Tables 6 and 7, respectively. This compound contains a six-atom nitrogen-containing heterocycle that has a manganese atom at the 2-position, methoxycarbonyl groups at the 3- and 4-positions, and a methyl group on the nitrogen atom. It could be viewed as a substituted N-methylpyridine, but the ring is decidedly nonplanar. Four carbon atoms (C(2), C(3), C(31) and C(32)) coordinated to the manganese atom Mn(1) form one plane, while a second plane is formed by the atoms C(2), C(5), N, and C(32). The dihedral angle between the two planes is 42.6°. Carbon C(5) is formally a carbone center (Mn(2)-C(5) = 2.016)(4) Å), and there is significant multiple bonding between the atoms C(5) and N (C(5)-N = 1.311(4) Å). Two distances (C(3)-C(31)) and C(31)-C(32)) are significantly shorter than the others: 1.409(5) and 1.420(6) Å vs 1.462(5), 1.470(5), and 1.469(5) Å for C(2)-C(3), C(2)-C(5), and C(32)-N, respectively. One carboxylate group is coordinated to the manganese atom Mn(2) to form a five-membered ring (Mn(2)-O(4) = 2.087(3) Å). Structurally, compound 4a is very similar to the com-

Table 5. Positional Parameters and B(eq) Values for 4a

atom	x	у	z	B (eq), Å ²
Mn(1)	0.59719(6)	0.18526(3)	0.64411(5)	2.94(3)
Mn(2)	0.17295(6)	0.09019(4)	0.73137(5)	3.07(3)
O (1)	0.7674(3)	-0.0099(2)	0.6942(3)	5.5(2)
O(2)	0.6028(3)	-0.0314(2)	0.7814(3)	4.8(1)
O(3)	0.6066(3)	0.1094(2)	0.8954(2)	4.1(1)
O(4)	0.3661(3)	0.1025(1)	0.8590(2)	3.4(1)
O(11)	0.8540(4)	0.2021(2)	0.8400(3)	5.5(2)
O(12)	0.4547(4)	0.3312(2)	0.6600(3)	6.8(2)
O(13)	0.7787(4)	0.2447(2)	0.5117(3)	6.9(2)
O (21)	0.2433(4)	-0.0730(2)	0.7032(2)	6.2(2)
O(22)	0.0269(4)	0.0504(2)	0.9036(3)	6.9(2)
O(23)	-0.0924(3)	0.0667(2)	0.5472(2)	5.4(2)
O(24)	0.1093(4)	0.2568(2)	0.7313(3)	6.8(2)
Ν	0.2948(3)	0.1367(2)	0.5388(2)	2.9(1)
C (1)	0.4740(4)	0.1067(2)	0.8252(3)	3.0(2)
C(2)	0.4610(4)	0.1109(2)	0.7078(2)	2.6(2)
C(3)	0.5603(4)	0.0708(2)	0.6589(3)	2.6(2)
C(4)	0.6575(4)	0.0069(2)	0.7118(3)	3.1(2)
C(5)	0.3083(4)	0.1165(2)	0.6416(3)	2.8(2)
C(6)	0.1590(4)	0.1500(2)	0.4523(3)	3.9(2)
C(7)	0.6215(5)	0.1025(3)	1.0119(3)	5.9(3)
C(8)	0.6891(6)	-0.0946(3)	0.8396(4)	6.1(3)
C (11)	0.7522(5)	0.1946(2)	0.7656(4)	3.7(2)
C(12)	0.5116(5)	0.2750(3)	0.6540(3)	4.1(2)
C(13)	0.7075(5)	0.2210(2)	0.5634(4)	4.2(2)
C(21)	0.2176(4)	-0.0120(3)	0.7156(3)	3.74(9)
C(22)	0.0814(5)	0.0662(3)	0.8374(4)	4.3(2)
C(23)	0.0104(5)	0.0768(2)	0.6197(4)	3.75(9)
C(24)	0.1346(5)	0.1940(3)	0.7353(4)	4.2(2)
C(31)	0.5368(4)	0.0890(2)	0.5461(3)	3.0(2)
C(32)	0.4291(4)	0.1459(2)	0.5077(3)	3.1(2)
Table 6. Intramolecular Distances for 4a ^a				
Mn(1)-	-C(2)	2.167(4) O	(2)-C(8)	1.449(5)
Mn(1)-	-C(3)	2.056(4) O	(3) - C(1)	1.327(5)
Mn(1)-	-C(11)	1.808(5) O	(3) - C(7)	1.438(5)
Mn(1)-	-C(12)	1.798(5) O	(4) - C(1)	1.237(5)
Mn(1)-	-C(13)	1.788(5) O	-C (av)	1.140(5)
Mn(1)-	·C(31)	2.073(4) N	-C(5)	1.311(4)

Mn(1) - C(3)	2.056(4)	O(3) - C(1)	1.327(5)
Mn(1) - C(11)	1.808(5)	O(3)-C(7)	1.438(5)
Mn(1) - C(12)	1.798(5)	O(4) - C(1)	1.237(5)
Mn(1) - C(13)	1.788(5)	0~C (av)	1.140(5)
Mn(1) - C(31)	2.073(4)	N - C(5)	1.311(4)
Mn(1) - C(32)	2.105(4)	N-C(6)	1.458(5)
Mn(2) - O(4)	2.087(3)	N-C(32)	1.469(5)
Mn(2)-C(5)	2.016(4)	C(1) - C(2)	1.450(5)
Mn(2) - C(21)	1.867(5)	C(2) - C(3)	1.462(5)
Mn(2) - C(22)	1.853(5)	C(2) - C(5)	1.470(5)
Mn(2) - C(23)	1.790(5)	C(3) - C(4)	1.488(5)
Mn(2) - C(24)	1.861(5)	C(3) - C(31)	1.409(5)
O(1) - C(4)	1.183(4)	C(31) - C(32)	1.420(6)
O(2) - C(4)	1.332(5)		

^a Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

pound 5 formed by the addition of $HC \equiv CCO_2Me$ to the enone complex A (eq 1).



On the basis of simple electron-counting procedures, complex 4a is formally zwitterionic with a positive charge on Mn(2) and a negative charge on Mn(1). Compound 4b is believed to be structurally analogous to 4a with a phenyl group bonded to the nitrogen atom in the place of the methyl group in 4a.

When **2a** was allowed to react with HC=CCO₂Me in the presence of UV irradiation, the compound $Mn_2(CO)_7[\mu-\eta^4-CN(Me)CHC(CO_2Me)C(CO_2-Me)]$ (**4c**) was obtained in 31% yield. Compound **4c** is

 Table 7. Intramolecular Bond Angles for 4a^a

		Ų	
C(2) - Mn(1) - C(3)	40.4(1)	C(3)-C(2)-C(5)	117.8(3)
C(2) - Mn(1) - C(31)	68.6(1)	Mn(1) - C(3) - C(2)	73.9(2)
C(2) - Mn(1) - C(32)	72.4(1)	Mn(1)-C(3)-C(4)	132.2(3)
C(3) - Mn(1) - C(31)	39.9(1)	Mn(1)-C(3)-C(31)	70.7(2)
C(3) - Mn(1) - C(32)	69.0(2)	C(2) - C(3) - C(4)	125.3(3)
C(31) - Mn(1) - C(32)	39.7(2)	C(2)-C(3)-C(31)	112.7(3)
O(4) - Mn(2) - C(5)	80.1(1)	C(4) - C(3) - C(31)	121.1(3)
C(4) = O(2) = C(8)	116.0(3)	O(1) - C(4) - O(2)	123.3(4)
C(1) - O(3) - C(7)	117.7(3)	O(1) - C(4) - C(3)	125.9(4)
Mn(2) - O(4) - C(1)	113.2(2)	O(2) - C(4) - C(3)	110.8(3)
C(5) - N - C(6)	126.0(3)	Mn(2) - C(5) - N	136.3(3)
C(5) - N - C(32)	117.0(3)	Mn(2) - C(5) - C(2)	111.9(2)
C(6) - N - C(32)	117.0(3)	N - C(5) - C(2)	111.8(3)
O(3) - C(1) - O(4)	121.3(3)	Mn(1) - C(31) - C(3)	69.4(2)
O(3) - C(1) - C(2)	117.1(3)	Mn(1) - C(31) - C(32)	71.4(2)
O(4) - C(1) - C(2)	121.6(4)	C(3)-C(31)-C(32)	112.8(4)
Mn(1) - C(2) - C(1)	121.9(3)	Mn(1) - C(32) - N	110.3(2)
Mn(1) - C(2) - C(3)	65.7(2)	Mn(1)-C(32)-C(31)	68.9(2)
Mn(1) - C(2) - C(5)	111.5(2)	N-C(32)-C(31)	116.6(3)
C(1) - C(2) - C(3)	122.4(3)	Mn-C-O (av)	178.2(3)
C(1) - C(2) - C(5)	110.8(3)		

 a Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.





believed to be analogous to 4a,b, but on the basis of its IR and ¹H NMR spectra alone, one is not able to distinguish between the two possible isomers 4c and 4c'.



However, in comparison with 5, we prefer the structure **4c**, where the carboxylate substituent is located next to the heteroatom.

Discussion

In our previous studies we showed that $Mn_2(CO)_9(NCMe)$ reacts with $EtO_2CC \equiv CCO_2Et$ by insertion of the alkyne into the metal-metal bond and coupling of one of the CO ligands to yield the metalated enone complex A.⁷ Similarly, treatment of the isocyanide complexes $Mn_2(CO)_9(CNR)$ (1a,b) with Me₃NO in NCMe followed by addition of $MeO_2CC \equiv CCO_2Me$ has yielded the metalated enimine complexes 2a,b by the insertion of the alkyne into the metal-metal bond and coupling to the CNR ligand (see Scheme 1). The presumed intermediate $Mn_2(CO)_9(NCMe)(CNR)$ is unstable, and we thus used it without isolation. We have

Metalated N-Substituted Pyridines

shown previously that the enone complexes are formed by the insertion of a CO ligand into a metal-carbon bond of a dimetalated olefin precursor complex.⁷ Similarly, we propose that the coupling of the isocyanides to the alkyne occurs by the insertion of the isocyanide into the metal-carbon bond of an unobserved dimetalated olefin intermediate. Small amounts of the isocyanide-containing metalated enone complexes **3a,b** were also obtained in these reactions. The higher yields of the complexes **2a,b** relative to complexes **3a,b** is believed to be due to the greater ability of isocyanides to insert into the metal-carbon bond than is the case for CO. This tendency has been observed previously for isocyanide insertion into other types of metal-carbon bonds.¹⁴

In the metalated enone complexes the oxygen atom of the C=O group is coordinated to one of the metal atoms. We found the nitrogen atom of the C=NR group is coordinated to one of the metal atoms in a similar fashion. The coordination of the oxygen atom in the enone complexes provided a condition that facilitated a novel 4 + 2 cycloaddition of alkynes to these complexes to produce metalated pyrans (eq 1) that could subsequently be freed from the metal atoms by treatment with a mixture of CO and HCl gases.

Likewise, we have found that the addition of alkynes to the compounds 2a,b in the presence of UV irradiation produces a similar 4 + 2 cycloaddition of the alkyne to the complexes to produce nitrogen-containing heterocycles in the form of the metalated N-substituted pyridine complexes 4a,b (eq 2). Solutions of 2a and



 $HC \equiv CH$ showed no evidence of reaction at room temperature over periods of up to 3.5 h. However, on exposure to UV irradiation the reactions were complete within 5 min. The irradiation almost certainly promotes the decarbonylation step, which may facilitate the alkyne coupling to the enimine grouping through an initial interaction of the alkyne with the metal atom.

We have attempted to remove and isolate the heterocycle by treatment with CO/HCl mixtures, but due to the very small quantities involved we have been unable to obtain complete characterizations of these compounds.

Acknowledgment. This research was supported by the Office of Basic Energy Science of the U.S. Department of Energy.

Supplementary Material Available: Tables of hydrogen atom positional parameters and anisotropic thermal parameters for **2a** and **4a** (5 pages). Ordering information is given on any current masthead page.

OM940703N

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