molecule as a model of the diphosphene (**1**) for the computation. The geometry optimizations were carried out with STO-3G,[20] 44-31G,[21] and 44-31G + polarization function on the phosphorus atom (44-31G*).[22] Table II shows the calculated results of phosphinidenes (H-$\ddot{P}$:), diphosphenes (*trans*- and *cis*-H—P=P—H),[23] diphosphyne (P≡P), and diphosphane (H_2P-PH_2). The 44-31G bond lengths are considerably larger than the corresponding experimental values. The basis set, therefore, is not adequate for the prediction of the geometries of the molecules. On the other hand, the geometries calculated at the 44-31G* level are in good accord with the experimental values. By comparison with theoretical values (P≡P, 1.85; P=P, 2.00; P-P 2.25) and the observed distance for **1a**, it is suggested that the phosphorus–phosphorus bond in **1a** has normal double-bond character. The observed larger bond angle (∠PPC, 102.8°) in **1a** than the optimized angle in *trans*-P_2H_2 might be attributed to the steric hindrance due to ortho-*tert*-butyl groups. The computation was carried out on a HITAC M-200H computer at the Institute for Molecular Science, Okazaki, Japan.

Acknowledgment. This work was supported in part by the Science Research Grant-in-Aid (543008 and 57540276) from the Ministry of Education, Science and Culture of Japan. We thank Dr. Ken Hirotsu at Osaka City University for helpful discussion and also thank Dr. Hiro-o Hamaguchi at the University of Tokyo for obtaining the Raman spectra of **1**.

Registry No. 1a, 79073-99-7; **1b**, 85028-85-9; **1c**, 85028-86-0; **1d**, 85028-87-1; **2**, 83115-12-2; **3a**, 79074-00-3; **3b**, 85028-88-2; **3c**, 6781-96-0; **3d**, 644-97-3.

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[19] Presented in part at the 10th Symposium on Organic Sulfur and Phosphorus Chemistry, Gifu, Japan, Jan 1982.

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Nucleophile Addition/Carbonylation with η^4-Dienetricarbonyliron(0) Complexes

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We recently reported that reactive carbanions will add to η^4-(1,3-diene)Fe(CO)$_3$ complexes and that the stable intermediate can be protonated with trifluoroacetic acid to give substituted alkenes.[3,4] The results were interpreted in terms of intermediates **1** (from the 1,3-cyclohexadiene complex **2**; see Scheme I) and implied attack of the anion at C-1 of the diene ligand, although a minor product arising from CO incorporation (**3**) suggested some tendency toward attack at C-2. We now report studies undertaken to determine if CO insertion can be the major process in the presence of external CO.

Scheme I

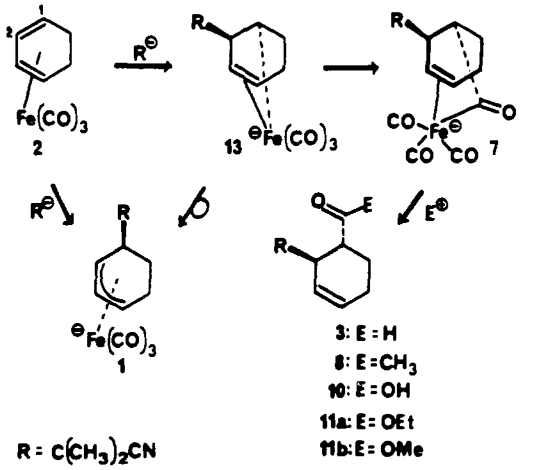
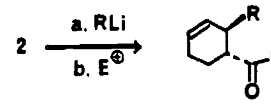


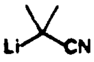
Table I. Reactions of **2** with Carbanions in the Presence of CO



entry	RLi	E⁺	E′	yield, %[b]
1	LiC(CH_3)$_2$CN	CF_3CO_2H	H	93[c]
2	LiC(CH_3)$_2$CN	CH_3I	CH_3	87[c]
3	LiC(CH_3)$_2$CN	O_2	OH	96[c]
4	LiC(CH_3)$_2$CN	$CH_3CH_2OSO_2F$	OCH_2CH_3	100[c]
5	LiC(CH_3)$_2$CN	CH_3OSO_2F	OCH_3	100[c]
6	Li*CH(CH_3)CN	CF_3CO_2H	H	77[c–e]
7	Li*CH(CH_3)CN	CH_3I	CH_3	83[d]
8	$LiCH_2CN$	CF_3CO_2H	H	81[e]
9	$LiCH_2CN$	CH_3I	CH_3	72[c]
10	LiC(CH_3)$_2$$CO_2$Et	$CH_3CH_2OSO_2F$	OCH_2CH_3	96[c]
11	LiC(CH_3)$_2$$CO_2$Et	CH_3I	CH_3	98[c]
12	Li*CH(CH_3)CO_2-*t*-Bu	$CH_3CH_2OSO_2F$	OCH_2CH_3	100[d]
13	$LiCH_2CO_2$-*t*-Bu	$CH_3CH_2OSO_2F$	OCH_2CH_3	42[c]
14	LiC(CH_3)$_2$$CO_2$Li	CF_3CO_2H	**18**[f]	
15	2-lithio-1,3-dithiane	CF_3CO_2H	H	58[e]

[a] For the general procedure, see ref 14. [b] The yields are based on distilled samples, homogeneous by GLPC and ^{13}C NMR data. [c] The structures are assigned as trans on the basis of selective proton-decoupling experiments in comparison with data for **9**. [d] This product was obtained as a mixture of epimers about the chiral carbon (denoted by the asterisks) in the carbanion unit. [e] This product was obtained as a mixture of cis and trans isomers. [f] This product was established to be the pure cis-anhydride **18** isomer based on proton-decoupling experiments, IR, and ^{13}C NMR spectral data (see ref 9).

When anion **4** is combined with complex **2**[5] under argon (−78 to +25 °C) and then exposed to CO at about 1.5 atm, protonation



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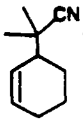

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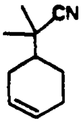

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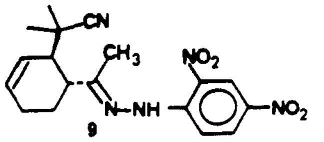

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[1] (a) Princeton University. (b) Merck Institute for Therapeutic Research.

[2] Trainee of the National Institutes of Health, 1980–1981. Exxon Fellow, Princeton University, 1982–1983.

[3] Semmelhack, M. F.; Herndon, J. W. *Organometallics*, in press.

[4] Preliminary partial accounts of this work based on lecture presentations have been published: (a) Semmelhack, M. F. *Pure Appl. Chem.* **1981**, *53*, 2379–2383. (b) Abstracts of the 131st National American Chemical Society Meeting, ORGN 21.

[5] **2** can be prepared via the general thermal or photochemical procedures: (a) Birch, A. J.; Cross, P. E.; Lewis, J.; White, D. A.; Wild, S. B. *J. Chem. Soc. A* **1968**, 332–340. (b) Von Gustdorf, K.; Pfaifer, A.; Grevels, F. W. *Z. Naturforsch.* **1971**, *266*, 66–67.

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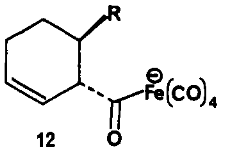
and isolation of the organic products gives only the alkenes **5** and **6**. No incorporation or other influence of CO is apparent. However, if CO is present at 1.4–1.5 atm during the mixing of anion **4** and complex **2** at −78 °C in THF/HMPA (4:1), an intermediate (we propose **7**) is formed and then protonated with trifluoroacetic acid to produce **3** in high yield. While the intermediate has not been isolated, the ^1H NMR spectrum of the solution before quenching with acid shows a pattern consistent with the proposed structure of **7**, including signals assigned to the olefinic protons at δ 3.90–4.00.[6] Similarly, the ^{13}C NMR spectrum shows two doublets (δ 58.35, 56.67) which we tentatively assign to the olefinic carbons. Structure **7** can be viewed as an analogue of the acyliron tetracarbonyl anions involved in Collman's reaction,[7] and we have shown that it undergoes parallel reactions. Addition of excess methyl iodide to a solution of **7** leads to methyl ketone **8** in 87% yield. The structure of **8** has been rigorously established by an X-ray diffraction study on the hydrazone **9** (supplementary material).[8,9] Similarly, the use of an oxidative isolation procedure[11] gives the carboxylic acid **10** in 96% yield.[9] We also converted **7** to the corresponding ethyl and methyl esters (**11**, 100% yields) by reaction with the appropriate alkyl fluorosulfonate followed by ferric chloride oxidation.[9,12]

The data presented so far require a transient intermediate interacting with CO, preventing formation of **1** (which appears not to incorporate CO). We consider three possibilities to be reasonable. First, the CO might induce formation of transient but highly reactive η^2-(1,3-cyclohexadiene)Fe(CO)$_4$, which would lead, in turn, to acyliron tetracarbonyl anion **12**. A second alternative is initial addition at C-2 of complex **2** to give homoallyl complex **13**.[14] This intermediate readily explains formation of **7** and might undergo iron migration (via β-hydride elimination/readdition) to the (presumably) more stable isomer, **1**. A third possibility is initial addition at C-2, followed by rapid rearrangement of the anion unit to C-1. Concerning the first possibility, structure **12** is inconsistent with the preliminary NMR data on the first stable intermediate (**7**).[6] In addition, we have demonstrated that exchange of the coordinated CO with the atmosphere of CO does not occur before or during the reaction with the anion.[13] The first mechanism implies 25% incorporation of external CO at the aldehyde carbon, wherein in the second and third possibilities the external CO simply fills the coordination sphere of the iron after insertion of one of the original CO ligands and allows no incorportation of external CO into the aldehyde carbonyl. In addition, if CO were promoting a fast $\eta^4 \rightleftarrows \eta^2$ interconversion, the unreacted (diene)iron tricarbonyl recovered would have incorporated the external CO.



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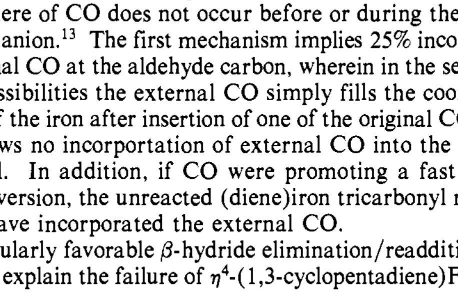
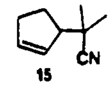
Particularly favorable β-hydride elimination/readdition (from **14**) may explain the failure of η^4-(1,3-cyclopentadiene)Fe(CO)$_3$[15] to undergo CO incorporation. Under the usual conditions with anion **4** and CO at 1.5 atm, the only products obtained are the substituted cyclopentenes **15** and **16** (72% yield).





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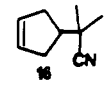

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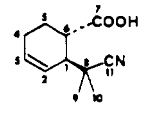
(6) In Me$_2$SO-d_6. No signals are detected downfield of δ 4.2. While we know no close analogy in other anionic iron–olefin systems; the upfield shift of ca 1.5 ppm (compared to the signals for olefinic protons in free cyclohexene) is consistent with an anionic complex.

(7) Collman, J. P. *Acc. Chem. Res.* **1975**, *8*, 342–347.

(8) The hydrazone was formed in the usual way (mp 153–154 °C). It was hydrolyzed[10] back to the same isomer (**8**) in order to establish that no structural change occurred during derivatization.

(9) The structures of products **3**, **10**, **11a**, **11b**, and the unnumbered products listed in the table were established by comparison of ^1H and ^{13}C NMR spectral data with corresponding data for **8**, for which the structure was established by the X-ray study on **9**. ^1H NMR data at 90, 270, and 500 MHz with extensive spin-decoupling procedures were used. As indicated in the footnotes to the table, most of the products were obtained in >98% purity by simple short-path distillation, as evidenced by GLPC analysis and ^{13}C NMR spectral data. Satisfactory IR, low-resolution MS, and analytical data (high resolution MS or combustion analysis) were obtained for all new compounds. Representative characterization data follow. **8**: IR (neat) 3040 (m, vinyl C–H), 2950 (s, C–H), 2250 (m, C≡N), 1720 (vs, C═O), 1660 (w, C═C), 1435 (s), 1365 (s), 1240 (m), 1225 (m), 1170 (s) cm^{-1}; ^1H NMR (90 MHz, CDCl$_3$) δ 5.81 (AB pattern of multiplets, 2 H, J = 12 Hz, H at C-1,2), 2.6–3.0 (m, 2 H, H at C-3,4), 2.27 (s, 3 H, H at C-12), 1.4–2.2 (m, 4 H, H at C-5,6), 1.52 (s, 3 H, CH$_3$), 1.48 (s, 3 H, CH$_3$); ^{13}C NMR (CDCl$_3$, H decoupled) δ 209, 130, 124, 123, 48, 42, 36, 28, 25, 24.3, 24.0, 23. **10**: ^1H NMR (CDCl$_3$, 500 MHz) δ −11.8 (s, 1 H, COOH), 6.00 (br d, 1 H, J = 10.0 Hz, H at C-3), 5.71 (dd, 1 H, J = 10.0, 1.4 Hz, H at C-2), 2.79 (m, 1 H, H at C-1), 2.65 (m, 1 H, H at C-6), 2.05 (m, 2 H, H at C-4), 2.02 (m, 1 H, H at C-5 cis to H at C-6), 1.81 (m, 1 H, H at C-5 trans to H at C-6), 1.38, 1.34 (2 s, 6 H, CH$_3$). Irradiated at δ 6.00: 5.71 (br d, J = 1.4 Hz), 2.79 (td, J = 9.3, 1.2 Hz), 2.65 (unaffected). Irradiated at δ 5.71: 6.00 (dt, J = 1.2 Hz), 2.79 (m), 2.65 (unaffected). Irradiated at δ 2.79: 6.00 (dt, J = 10.0, 1.4 Hz), 5.71 (br d, J = 10.0 Hz), 2.65 (dd, J = 9.5, 1.2 Hz). Irradiated at δ 2.65: 6.00, 5.71 (unaffected), 2.79 (br s). Irradiated at δ 2.05: 6.00 (dd, J = 10.0, 0.8 Hz), 5.71 (dd, J = 10.0, 1.4 Hz), 2.79 (br s), 2.65 (td, J = 9.5, 1.2 Hz). Irradiated at δ 2.02: 6.00 (dd, J = 10.0 Hz), 5.71 (dd, J = 10.0, 1.4 Hz), 2.79 (unaffected), 2.65 (t, J = 9.5 Hz). Irradiated at δ 1.81: 6.00, 5.71, 2.79 (unaffected), 2.65 (m). ^{13}C NMR (CDCl$_3$) δ 182.0 (s, COOH), 130.4, 123.8 (2d, vinyl C), 124.2 (s, C≡N), 43.1, 41.0 (2d, C-1,6), 36.1 (s, C-8), 25.2, 24.6, 24.0, 24.8 (C-4,5,9,10). IR (neat) 2200–3500 (vs, O–H), 2230 (m, C≡N), 1700 (s, C═O), 1450 (m), 1430 (m), 1390 (m), 1300 (s), 1180 (s), 950 (s) cm^{-1}. The coupling constant between the H's at C-1,6 is 9.5 Hz, consistent with a trans orientation.



10

(10) The general procedure was due to the following: McMurry, J. E.; Silvestri, M. *J. Org. Chem.* **1975**, *40*, 1502–1504.

(11) For the general oxidative isolation procedure, see: Collman, J. P.; Winters, S. R.; Komoto, R. G. *J. Am. Chem. Soc.* **1973**, *95*, 249–250.

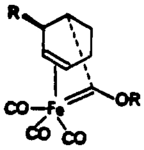
(12) The reaction mixture was diluted with acetone at 24 °C, and solid ferric chloride hexahydrate was added portionwise until gas evolution was no longer noticeable (10–30 min).

(13) For example, when complex **2** is dissolved in THF under ^{13}CO (90% ^{13}C) at temperatures ranging from −78 to +160 °C, the complex can be recovered without significant (<1%) incorporation of the label. When irradiated at 25 °C with a medium-pressure mercury arc through Pyrex, the same mixture gave 15% incorporation of ^{13}CO. In a similar experiment where **2** was mixed with 0.5 mol equiv of anion **4**, under the standard conditions[16] for addition/carbonylation/protonation, the usual product (**3**) was obtained with <1% incorporation of ^{13}C at aldehyde carbon (^{13}C NMR peak enhancement). Rapid intramolecular equilibration (site exchange) of CO ligands in complexes such as **2** has been established: Bischofberger, P.; Hansen, H.-J. *Helv. Chim. Acta* **1982**, *65*, 721–725.

(14) We are aware of no published example of an iron complex with structure closely related to **13**. Addition at C-2 is not predicted by the general correlation theory of nucleophilic addition to coordinated polyenes: Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, *34*, 3047–3077. However, their analysis is described for complexes carrying a positive charge and does not necessarily apply to the uncharged iron system. Detailed ab initio computations on η^4-(1,3-butadiene)Fe(CO)$_3$ show that the more electron-deficient sites on the diene ligand are at C-2 and C-3: (a) Connor, J. A.; Derrick, L. M. R.; Hall, M. B.; Hillier, I. H.; Guest, M. F.; Higginson, B. R.; Lloyd, D. R.; *Mol. Phys.* **1974**, *23*, 1193–1205. (b) El-Awady, A. A. *J. Inorg. Nucl. Chem.* **1974**, *36*, 2185–2190. In addition, it has been established that electrophilic addition occurs preferentially at C-1 and C-4 of the 1,3-diene ligands: Graf, R. E.; Lillya, C. P. *J. Organomet. Chem.* **1979**, *166*, 53–62. We have in progress a series of experiments with substituted 1,3-dienes that demonstrate that addition at C-2 is generally the kinetically favored process: J. W. Herndon and Hanh T. M. Le, unpublished results.

(15) Kochbar, R. K.; Pettit, R. *J. Organomet. Chem.* **1966**, *6*, 272–278.

Table I displays the results of a systematic study of complex **2** with a variety of carbanions in the presence of CO.[16] Ketone enolates are apparently not reactive enough to give useful efficiency, but more reactive carbon nucleophiles produce high yields of carbonyl products. The formation of the trans isomer in most cases is consistent with the addition of the nucleophile from the anti direction,[17] followed by CO insertion with retention at the migrating carbon.[7,18] The formation of esters after reaction with the alkyl fluorosulfonates and oxidation is reminiscent of the chemistry of acylchromium pentacarbonyl anions[19] but is not generally observed for the iron analogue.[20] We propose that an (alkylidene)iron intermediate (**17**) forms by O-alkylation of the proposed acyliron tricarbonyl anion **7** and is oxidized readily to give the esters **11**. Systematic study of this proposal is underway. Under the strong acid quenching conditions, mixtures of cis- and trans-disubstituted cyclohexenes are usually obtained (Table I, entries 1, 6, 8, 14, and 15). These results can be explained by epimerization during acid quenching, giving an equilibrium mixture. In the special case of dilithioisobutyrate (entry 14), ferric chloride treatment appears to oxidize the expected carboxylic acid aldehyde into an anhydride (**18**), and epimerization allows exclusive formation of the cis ring fusion isomer.[9] However, with other quenching techniques, using carbon electrophiles, the pure trans-3,4-disubstituted cyclohexenes are obtained.



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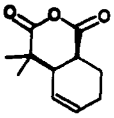
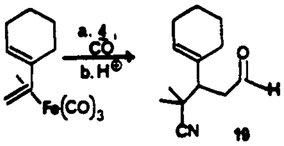
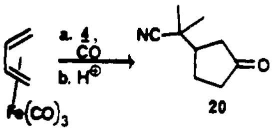


18

The carbonylation process appears to be quite general. For example, the complex from 1-vinylcyclohexene[21] reacts with **4** and CO to give, after protonation, the aldehyde **19** in 71% yield.[9] With other open chain dienes, preliminary results suggest further reaction of the acyliron intermediates can occur. Under the usual conditions, η^4-(1,3-butadiene)Fe(CO)$_3$[5b] leads to the 3-substituted cyclopentanone **20** in 76% yield.[22] Further development of these processes is underway.





Acknowledgment. We are pleased to acknowledge support of this work through a research grant from the National Science Foundation (CHE-7905561) and through a graduate traineeship from the Public Health Service to J.W.H. In addition, NMR facilities at Princeton and Yale, provided partly by grants from the National Science Foundation, were employed in this project.

Supplementary Material Available: Spectral and X-ray data for **9** (4 pages). Ordering information is given on any current masthead page.

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[16] The general procedures for experiments reported in the table follow. Into a stirred solution of the carbanion (2.7 mmol) in a mixture of THF and HMPA (4:1, v:v; 10 mL) at -78 °C under argon was passed via syringe needle a stream of carbon monoxide for a period of 1 min, and then the closed system was pressurized to ca. 8 psi as measured by a regulator at the CO cylinder. The system was sealed by means of stopcocks held in place by rubber bands. The neat liquid η^4-(1,3-cyclohexadiene)iron tricarbonyl was added via syringe over 20 s. The mixture was stirred at -78 °C for 1 h and then at 25 °C for 1 h. After the mixture was cooled to -78 °C and the pressure was released, the intermediate was quenched with either excess trifluoroacetic acid (-78 to 25 °C over 10 min), methyl iodide (2 h at 25 °C), alkyl fluorosulfonate/ferric chloride (-78 to 25 °C), or oxygen/ferric chloride.[12] Filtration of the crude organic product through a short column of silica gel (eluting with hexane/dichloromethane) followed by short-path distillation gave the products listed in the table.

[17] No evidence for the direction of addition of nucleophiles to 1,3-diene ligands has been presented, but anti addition is general for alkene, allyl, cyclohexadienyl, and arene ligands. For a general discussion, see: Collman, J. P.; Hedgedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; pp 303-306.

[18] For a general discussion, see the book cited in ref 17, pp 264-266.

[19] For a general discussion, see: Casey, C. A. In "Transition Metal Organometallics in Organic Synthesis"; Alper, H., Ed.; Academic Press: New York, 1976; p 225.

[20] In general, acyliron tetracarbonyl anions are alkylated at iron (Collman's reaction). The one systematic study of alkylation with alkylating agents of the type used here failed to provide significant yields of the iron-alkylidene species: Fischer, E. O.; Beck, H.-J.; Kreiter, C. G.; Lynch, J.; Müller, J.; Winkler, E. *Chem. Ber.* **1972**, *105*, 162-172. However, phosphine-substituted analogues have been converted to (alkylidene)iron complexes in high yield: Condor, H. L.; Darensbourg, M. *Inorg. Chem.* **1974**, *13*, 506-511.

[21] Dauben, W. G.; Lorber, M. E. *Org. Mass Spectrosc.* **1970**, *3*, 211-218.

[22] Cyclopentanone **20** was isolated by short-path distillation (80-110 °C (0.8 torr)): ^{1}H NMR (CDCl$_3$) δ 1.6-2.2 (m, 7 H), 1.34 (s, 3 H), 1.30 (s, 3 H); ^{13}C NMR (CDCl$_3$) δ 2.5.5 (s), 122.7 (s), 45.4 (d), 40.6 (t), 38.2 (t), 25.4 (t), 35.9 (s), 25.1 (q), 24.3 (q); IR (neat) 2980 (s), 2900 (m), 2240 (m), 1740 (s), 1460 (m), 1405 (m), 1395 (m), 1370 (m), 1260 (s) cm^{-1}; GC-MS, *m/z* 151 (parent, 7), 89 (3), 83 (38), 69 (5), 56 (9), 55 (100). Anal. Calcd for $C_9H_{13}N$: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.55; H, 8.68; N, 9.09.

Mechanism of Ligand Substitution in $Mn_2(CO)_{10}$

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By a metal isotope double-labeling procedure, we[1] recently established that thermally initiated ligand substitution reactions of $Re_2(CO)_{10}$ do not involve Re-Re bond cleavage; rather the CO predissociation step $Re_2(CO)_{10} \rightleftharpoons Re_2(CO)_9 + CO$ followed by ligand addition to $Re_2(CO)_9$ precisely describes the mechanism. We have now established that $Mn_2(CO)_{10}$ substitution reactions[2] are mechanistically analogous to the rhenium systems. These experiments suggest that the Mn-Mn bond energy in $Mn_2(CO)_{10}$ is probably greater than the earlier *estimates*[3,4] of 16-22 kcal/mol.

Our experiments with ^{13}CO substitution in $Mn_2(CO)_{10}$ in octane solution at 120 °C and 550-660 torr of ^{13}CO establish a reaction fully consistent[5] with eq 1 and a half-life of 45 ± 10 min as

$$Mn_2(CO)_{10} \xrightleftharpoons{-CO} Mn_2(CO)_9 \xrightleftharpoons{^{13}CO} Mn_2(CO)_9(^{13}CO) \quad (1)$$

compared to a half-life[6a] of 46 min for $P(C_6H_5)_3$ substitution (Figure 1, supplementary material). To enable an incisive[7] test of thermally initiated Mn-Mn bond scission by a double-labeling procedure under conditions of ligand exchange, $Mn_2(CO)_{10}$ and $Mn_2(^{13}CO)_{10}$ were physically mixed and then reacted in octane with ^{12}CO or with ^{13}CO at 120 °C. Mass spectrometric analysis of the reaction mixture after varying reaction times evinced no evidence (i.e., buildup of $Mn_2(^{12}CO)_{6-4}(^{13}CO)_{4-6}$ molecules, 394-396 amu range, was less than ~3%) that scission of the Mn-Mn bond occurs at significant rates under these conditions of relatively rapid CO exchange (Figure 1). Thus CO ligand

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[1] Stolzenberg, A. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1983**, *105*, 822.

[2] For a summary of studies and conclusions regarding $Mn_2(CO)_{10}$ ligand substitution reactions see: Muetterties, E. L.; Burch, R. R.; Stolzenberg, A. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 89-118.

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[4] Connor, J. A.; Zafarani-Moattar, M. T.; Bickerton, J.; El Saied, N. I.; Suradi, S.; Carson, R.; Al Takhin, G.; Skinner, H. A. *Organometallics* **1982**, *1*, 1166-1174.

[5] Assuming a first-order dissociative process with successive dissociation rates statistically corrected for the number of ^{12}CO groups remaining and that replacement of bound ^{13}CO by ^{12}CO is insignificant, the problem is analyzable by a ten-step radioactive decay chain (cf. ref 1). The agreement between experiment and theory was good (Figure 1, supplementary material).

[6] (a) Wawersik, H.; Basolo, F. *Inorg. Chim. Acta* **1969**, *3*, 113. (b) Atwood, J. D. *Inorg. Chem.* **1981**, *20*, 4031 and references therein. (c) Schmidt, S.; Basolo, F.; Trogler, W. *Inorg. Chem.* **1982**, *21*, 1698.

[7] A metal-based isotopic double-labeled procedure is not feasible for manganese because there is only one stable manganese isotope.

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