lization by interaction with the Li^+ cation. A hydride ligand of the $Re(\mu\text{-}H)_2Re$ moiety (which has a marked H^- polarization[8]) then migrates from the cluster to the formylic carbon atom, giving the CH_2O group, stabilized by the μ-coordination of the oxygen atom on a cluster edge.

Two experiments gave support to this mechanism. (i) On performing the reaction on a sample of **1** selectively enriched (ca. 45%) in ^{13}CO at the carbonyls mutually trans of the $Re(CO)_4$ moiety,[10] the two by far most intense signals in the ^{13}C NMR spectrum were at δ 52.5 (t, $^1J_{CH}$ = 134 Hz) and 200, due to the CH_2O group and to the carbonyl trans to it, respectively. (ii) The formyl intermediate was observed on performing the reaction in a NMR tube at −40 °C:[11] a signal at δ 15.3 was detected, together with the hydridic resonances expected for a $[Re_3(\mu\text{-}H)_4(CHO)(CO)_9]^{2-}$ unsaturated species (Figure 1a).

The structure of $[Re_3(\mu\text{-}H)_3(\mu_3\text{-}\eta^2\text{-}CH_2O)(CO)_9]^{2-}$ (**3**), as the $[NEt_4]^+$ salt, has been investigated by X-ray analysis.[12] The dianion (Figure 2) contains an isosceles Re_3 triangle and shows an overall idealized C_s—m symmetry, the mirror plane passing through Re1, the C and O atoms of the bridging group, and the middle point of the Re2–Re3 edge. Each rhenium atom bears three terminal carbonyls, and three hydrides, not directly located, are supposed to bridge the three triangular edges on the basis of the values of the M–M bond lengths and of the ligand stereochemistry. Within the CH_2O group the value of the C–O bond distance [1.467 (12) Å] is close to that expected for a single bond, and the value of the Re1–C–O angle [106.0 (8)°] and of the other angles at carbon, involving the H atoms and therefore affected by high uncertainties [range 100 (6)–117 (5)°, mean 110°], are indicative of an sp^3 hybridization.

This dihydrogenated CO ligand, clearly stabilized by interaction with different metal centers, confirms the previous suggestions of the intermediate role of a bridging oxymethyl group in the reductive hydrogenation of CO in homogeneous catalytic systems and can also represent a valid model of intermediates on metal surfaces.

Treatment of the oxymethyl complex with stoichiometric CF_3SO_3H, at −80 °C, in anhydrous THF, gives almost quantitatively a species identified by NMR analysis as the anion $[Re_3(\mu\text{-}H)_3(\mu_3\text{-}\eta^2\text{-}CH_2OH)(CO)_9]^-$ (**4**), in which the hydroxymethyl group maintains the same coordination mode as the parent ligand (see Scheme I).[13] The resonances of the hydrides (at δ −9.15 (1) and −12.25 (2), values close to those of **3**) indicate in fact a C_s symmetry for the anion. The hydroxylic hydrogen gives a signal at δ 9.78 (which exchanges with D_2O), while the resonances of the CH_2 group are downfield shifted with respect to **3**, due to the protonation of the oxygen atom [^1H NMR δ 6.27 (2); ^{13}C NMR δ 74 (t, $^1J_{CH}$ = 139 Hz)].

This anion is stable in solution up to −40 °C. At higher temperatures it decomposes to unidentified products. When the temperature is raised under CO flow, however, the main species formed (40–60%) is the anion $[Re_3(\mu\text{-}H)_2(CO)_{12}]^-$, which is also the principal component of the reaction mixtures obtained on performing the protonation reaction directly at room temperature under CO.[14] A possible pathway to this species involves reductive elimination of CH_3OH from an unstable η^1-bonded hydroxymethyl intermediate. The presence of methanol, in concentration corresponding to that of $[Re_3(\mu\text{-}H)_2(CO)_{12}]^-$, has been ascertained by gas chromatographic analysis.[15] Moreover, when a sample of **3** selectively enriched in ^{13}C at the oxymethyl carbon was used, ^{13}C-enriched methanol was obtained.

The speculation that H_2 could replace the successive action of H^- and H^+, according to the overall reaction

$$[Re_3(\mu\text{-}H)_4(CO)_{10}]^- + H_2 + 3CO \rightarrow [Re_3(\mu\text{-}H)_2(CO)_{12}]^- + CH_3OH$$

is, at present, an attractive working hypothesis.

Acknowledgment. We thank the Italian CNR "Progetto strategico: Dinamica molecolare e catalisi" for financial support.

Supplementary Material Available: Crystallographic experimental details and tables of positional and thermal parameters and bond lengths and angles (7 pages); a listing of structure factors (12 pages). Ordering information is given on any current masthead page.

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(10) Such a sample was obtained by treating with ^{13}CO (ca. 90%) a solution of the anion $[Re_3(\mu\text{-}H)_4(CO)_9(NCMe)]^-$, in which a labile nitrile replaced one of the two trans diaxial CO ligands of compound **1**. Beringhelli, T.; Ciani, G.; D'Alfonso, G.; Molinari, H.; Sironi, A. *J. Chem. Soc., Dalton Trans.*, in press.

(11) A 25-mg (0.026-mmol) sample of $[Re_3H_4(CO)_{10}][NEt_4]$ in a 5-mm NMR tube, dissolved in THF-d_8 (distilled over Na/benzokethyl), was treated at −80 °C with 40 μL of a 1 M solution of $Li[BH(s\text{-}Bu)_3]$ in THF. ^1H NMR spectra (−40 °C) showed the appearance of signals at δ 15.3 (1), −7.75 (1), −7.95 (1), and −10.79 (2). When the formyl concentration reached ca. 40% of the starting compound (ca. 2 h), the resonances of compound **3** appeared and increased in intensity.

(12) Crystal data: $C_{26}H_{45}N_2O_{10}Re_3$, M_r 1104.3; crystal size 0.14 × 0.33 × 0.39 mm; orthorhombic, space group $P2_12_12_1$ (No. 19), with a = 9.676 (3), b = 16.348 (5), c = 21.709 (5) Å; U = 3433.9 Å^3; Z = 4, D_{calcd} = 2.13 g cm^{-3}; μ(Mo Kα) = 107.0 cm^{-1}; Mo Kα radiation (λ = 0.71073 Å); diffractometer Enraf-Nonius CAD4. The refinements were carried out by full-matrix least-squares, on the basis of 2374 significant [$I > 3\sigma(I)$] unique data. The final values of the agreement indices for the correct enantiomorph are R = 0.027 and R_w = 0.031.

(13) The only other alternative consistent with the C_s symmetry—namely, protonation on the oxygen atom of the carbonyl trans to the CH_2O group—seems most unlikely for the low shift (less than 2 ppm upfield) undergone by the ^{13}C resonance of this carbonyl.

(14) This species, identified spectroscopically, was also isolated by crystallization from the reaction mixture. Churchill, M. R.; Bird, P. H.; Kaesz, H. D.; Bau, R.; Fontal, B. *J. Am. Chem. Soc.* **1968**, *90*, 7135. The only other known hydridic species present in significant concentration (10–30%) was the anion $[Re_3(\mu\text{-}H)_3(\mu\text{-}OCH_3)(CO)_{10}]^-$, identified spectroscopically. Ciani, G.; Sironi, A.; D'Alfonso, G.; Romiti, P.; Freni, M. *J. Organomet. Chem.* **1983**, *254*, C37.

(15) After completion of the reaction, the solvent was removed under vacuum, trapped, and analyzed on a Porapak QS column, at 150 °C.

Synthesis, CO Substitution, and Structure of Tricarbonyl(η^5-3,4-dimethylpyrrolyl)manganese(I). Evidence for Slippage toward Nitrogen of the N-Heterocycle

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Summary: The compound tricarbonyl(η^5-3,4-dimethylpyrrolyl)manganese(I) (**2**) and its corresponding 2,5-dimethylpyrrolyl (**3**) compound were synthesized for the first time, and the X-ray structure of **2** and kinetic data support a mechanism which involves $\eta^5 \rightarrow \eta^3$ slippage toward N for CO substitution reactions.

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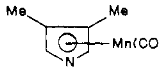
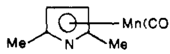
(1) (a) Northwestern University. (b) University of Delaware.

Table I. Rates of CO Substitution by P(n-Bu)$_3$ for the η^5-Pyrrolyl Complexes in Decalin at 130 °C

complex	no.	k, m^{-1} s^{-1}
	1	3.88×10^{-4}
	2	1.86×10^{-4}
	3	1.24×10^{-6}

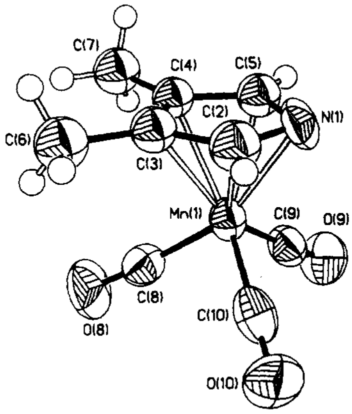


Figure 1. Molecular structure and labeling scheme for one of two independent molecules of [η^5-$C_4(CH_3)_2H_2N$]Mn(CO)$_3$. The two molecules are chemically indistinguishable; molecule 2 is numbered as ten plus the numbering of molecule 1. Some important bond distances (Å) Mn(1)–N(1), 2.11 (1); Mn(1)–C(2), 2.09 (1); Mn(1)–C(3), 2.17 (1); Mn(1)–C(4), 2.18 (1); Mn(1)–C(5), 2.10 (1); N(1)–C(2), 1.36 (1); C(2)–C(3), 1.40 (2); C(3)–C(4), 1.41 (1); C(4)–C(5), 1.41 (2); and C(5)–N(1), 1.37 (1). Librational correction lengthened all values by ~0.01 Å.

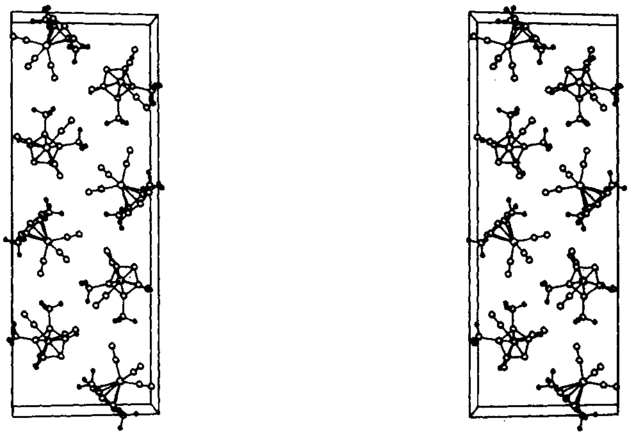
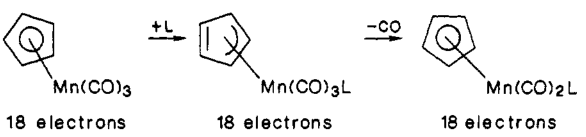


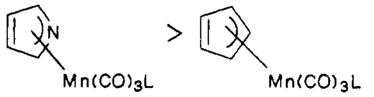
Figure 2. Stereoview of the unit-cell packing for [η^5-$C_4(CH_3)_2H_2N$]Mn(CO)$_3$ as viewed down the a axis (b vertical).

There continues to be an interest[2] in reactions of cyclopentadienyl and of indenyl metal complexes believed to involve $\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$ ring slippage. Such processes enhance ligand substitution reactions, so important in homogeneous catalysis, by localizing a pair of electrons on the ring which permits a nucleophilic attack on the metal. This then results in a low-energy associative reaction[3] pathway involving an 18-electron active intermediate (eq 1).



(1)

Recently we[4] reported a kinetic study of CO substitution of the pyrrolyl compound (η^5-C_4H_4N)Mn(CO)$_3$, which is estimated to react about 10^8 times faster than the cyclopentadienyl compound (η^5-C_5H_5)Mn(CO)$_3$. The large rate enhancement was attributed to N being more electronegative than C, resulting in a greater tendency for electron withdrawal from the metal by the N heterocycle relative to the carbocycle. Another factor to consider is that the 2-azaallyl group I may be more stable than the allyl group II. There is nuclear quadrupole resonance evidence[5] that



I II

the parent compound (η^5-C_4H_4N)Mn(CO)$_3$ should be viewed as an azaallylic–olefinic system similar to I. However, a more recent ^{13}C NMR study[6] indicates that this asymmetric bonding mode may be incorrect.

In an attempt to get more information relative to the importance of I, we have prepared[7] compounds **2** and **3** for the first time, and determined the rates of CO substitution of these complexes (Table I). The results show, as expected,[9] that the rates of reaction of the dimethyl derivatives **2** and **3** are less than that of the parent **1**. However, the important observation is that **2** reacts 10^2 times faster than does **3**, in accord with steric retardation of the formation of I having N at the center of the allyl group.

Additional support of the importance of structure I is provided by the X-ray structure of **2**. Compound **2** crystallizes with two independent molecules forming the crystallographic asymmetric unit.[10] To the limits of

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(2) (a) Shuster-Wolden, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657–1663. (b) Casey, C. P.; Jones, W. D. *J. Am. Chem. Soc.* **1980**, *102*, 6154–6156. (c) Ji, L.-N.; Rerek, M. E.; Basolo, F. *Organometallics* **1984**, *3*, 740–745. (d) Faller, J. W.; Crabtree, R. H.; Habib, A. *Organometallics* **1985**, *4*, 929–935. (e) Yang, G. K.; Bergman, R. G. *Organometallics* **1985**, *4*, 129–138. (f) merola, J. S.; Kacmarcik, R. T.; Van Engen, D. *J. Am. Chem. Soc.* **1986**, *106*, 329–331.

(3) Basolo, F. *Inorg. Chim. Acta* **1985**, *100*, 33–39.

(4) Ji, Liang-Ni; Kershner, D. L.; Basolo, F. *J. Organomet. Chem.* **1985**, *296*, 83–94.

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(6) Efraty, A.; Jubran, N.; Goldman, A. *Inorg. Chem.* **1982**, *21*, 868–873.

(7) (a) The 3,4-dimethylpyrrole[8] (0.80 g, 8.4 mmol) and $Mn_2(CO)_{10}$ (3.0 g, 7.7 mmol) (Strem) were refluxed in dry xylene under a N_2 atmosphere for 4 h at which time no further changes in the ν_{CO} region of the IR occurred. The xylene was removed under reduced pressure, dry pentane was added to the residue, and the mixture was suction filtered through a sintered glass frit. The resultant orange solution was concentration under reduced pressure and subsequently chromatographed on Al_2O_3 (Alcoa Chemicals). Elution with pentane yielded first $Mn_2(CO)_{10}$ and then the product. The orange-yellow crystalline product was obtained by placing a pentane solution of the product in a freezer (–25 °C) overnight: yield 0.85 g (3.7 mmol, 44%); IR (cm^{-1}, ν_{CO}, decalin) 2035, 1962, 1944; ^{1}H NMR ($CDCl_3$) |δ 5.88 (H_a), 1.94 (Me); ^{13}C NMR ($CDCl_3$, –55 °C)| δ 105.91 (C_α), 105.32 (C_β), 10.24 (Me), 223.51 (CO); mass spectrum, m/e (relative intensity) M^+ 233 (206), $(M - CO)^+$ 205 (7.5), $(M - 2CO)^+$ 177 (32.1), $(M - 3CO)^+$ 143 (100). Anal. Calcd for $C_9H_8MnNO_3$: C, 46.37; H, 3.47; N, 6.01. Found: C, 46.27; H, 3.59; N, 6.02. (b) The synthesis of the tricarbonyl(η^5-2,5-dimethylpyrrolyl)manganese(I) is similar to that of **2**.

(8) Ichimura, K.; Ichikawa, A.; Imamura, K. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1157–1158.

(9) Rerek, M. E.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 5908–5912.

precision in this study (~±0.01 Å and ±0.5°), the two molecules are identical; one of the molecules is shown in Figure 1, and the lattice arrangement is shown in a stereoview in Figure 2. The pyrrole rings are planar (maximum deviation = 0.005 Å) and perpendicular (tilt angle = <1°) to the rotation cone created by the $Mn(CO)_3$ pedestal. The molecule possesses near mirror-plane symmetry defined by the atoms N(1), Mn(1), C(8), O(8), and the midpoint of the C(3)–C(4) bond. The recently redetermined structure[11] of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ showed only a narrow range of Mn–C(ring) distances: 2.145 (2)–2.155 (2) Å. We find for the 3,4-dimethylpyrrolyl complex a much greater range 2.12 (1)–2.20 (1) Å (both sets with rigid-body librational corrections). The values at the short end of the range are the Mn(1)–N(1), Mn(1)–C(2), and Mn(1)–C(5) distances, and the long distances are the Mn(1)–C(3) and Mn(1)–C(4) bonds. This pattern represents some slippage[12] of the ring centroid toward N(1) by 0.060 Å from the intersection of the ring and the Mn–ring perpendicular vector.

All previously reported structures of $(\eta^5$-pyrrolyl$)Mn(CO)_3$ complexes have contained N-coordinated metallic groups.[13] Where error limits have been low enough to permit at least a 0.03-Å discrimination, the same ring slippage is seen, although to a lesser extent. Since none of the previously determined $(\eta^5$-pyrrolyl$)Mn(CO)_3$ complex structures were corrected for librational effects, it is difficult to make precise comparisons.

The C–N ring bonds, 1.37 Å (average), are shorter than the C–C ring bonds, 1.41 Å (average). Within the estimated standard deviations of these parameters (and for the previously reported N-coordinated pyrrole complexes) no indication exists for either diene or allyl–ene localization within the ring.

The $Mn(CO)_3$ group conforms closely to that found in $(\eta^5\text{-}C_5H_5)Mn(CO)_3$.[11] Unfortunately, we are unable to compare the X-ray structure of **2** with that of **3** because it formed an oil.

The results of this investigation show the subtlety of factors that affect rates of ligand substitution of transition-metal organometallic complexes. Work in progress on such factors will be reported in more detail later.

Acknowledgment. We thank the National Science Foundation and the donors of the Petroleum Research Foundation, administered by the American Chemical Society, for support of this research. D.L.K. thanks the graduate school at Northwestern University for a fellowship.

Supplementary Material Available: Tables atomic coordinates, bond distances, bond angles, anisotropic temperature factors, and hydrogen atom coordinates (5 pages); a listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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[10] Crystallographic data: $C_9H_8MnNO_3$, monoclinic, $P2_1/n$, $a = 6.578$ (2) Å $b = 29.285$ (7) Å, $c = 10.910$ (3) Å, $\beta = 99.88$ (2)°, $V = 2070.3$ (7) Å^3, $Z = 8$, D(calcd) = 1.495 g cm^{-3}, μ(Mo Kα) = 12.0 cm^{-1}, $T = 293$ K. All crystals examined showed evidence of a progressive, nondestructive phase transformation; jagged, stepped boundaries between phases moved with time, suggesting a defect or impurity nucleated process. The specimen chosen for data collection (0.28 × 0.32 × 0.44 mm), grown from pentane, was cleaved from a larger specimen and appeared to be a single phase. The crystal was multiply layered with epoxy cement to prevent sublimation. Intensity data were collected (Nicolet R3m) rapidly (6–20° min^{-1}) to the limit of observation ($2\theta = 45°$). Decay in I was less than 2%. Merging 2938 data yielded 2703 unique data ($R_{int} = 2.6\%$) of which 1242 with $F_o \geq 3\sigma(F_o)$ were considered observed. The structure was solved by direct methods and completed by difference Fourier syntheses. The asymmetric unit consists of two molecules of $(\eta^5\text{-}C_4(CH_3)_2H_2N)Mn(CO)_3$. Due to the small fraction of observed data, the carbon atoms of the rings and methyl groups were isotropically refined; the remaining non-hydrogen atoms were anisotropically refined. Hydrogen atoms were treated as idealized, isotropic contributions: C–H = 0.96 Å, $R_F = 5.45\%$, $R_{wF} = 6.33\%$, GOF = 1.21, $\Delta/\sigma = 0.06$, $\Delta(\rho) = 0.41$ e Å^{-3}, and $N_o/N_v = 6.4$. SHELXTL (5.1) software was used for all calculations (Nicolet Corp., Madison, WI).

[11] Fitzpatrick, P. J.; Page, Y. L.; Sedman, J.; Butler, I. S. *Inorg. Chem.* 1981, *20*, 2852.

[12] Faller, J. W.; Crabtree, R. H.; Habib, A. *Organometallics* 1985, *4*, 929–935.

[13] Pyshnograeva, N. I.; Setkina, V. N.; Andianov, V. G.; Struchkov, Yu. T.; Kursanov, D. N. *J. Organomet. Chem.* 1977, *128*, 381; 1978, *157*, 431; 1980, *186*, 331; 1981, *206*, 177; 1981, *209*, 169.

A New Method for the Preparation of Monofluorophosphane Complexes. Isolation of $[(CO)_5CrP(NEt_2Me)Et_2][BF_4]$[1]

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Summary: Complexed aminophosphane ligands undergo a single NR_2/F exchange on reaction with $[Me_3O][BF_4]$; for instance, $(CO)_5CrP(NEt_2)_3$ yields $(CO)_5CrPF(NEt_2)_2$. With $(CO)_5CrPEt_2NEt_2$, however, the ammoniophosphane complex $[(CO)_5CrP(NEt_2Me)Et_2][BF_4]$ is formed.

The first step in the acid cleavage of complexed aminophosphanes consists in the protonation of the nitrogen, thereby forming ammoniophosphane complexes.[2] There have been attempts to isolate these intermediates, but only products contaminated by ammonium salts[3,4] could be obtained. They have been characterized by NMR spectroscopy in one case.[3] Quite recently, the protonation of a complexed tricyclic aminophosphane led to an analytically pure substance.[5] It is reasonable that the reaction stops at this stage because of the great stability of the cyclic ligand and that cleavage of the P–N bond does not occur as a consequence. The protonated complex behaves as a strong acid and reacts with bases to yield the starting complex.

These results suggest that the reason why the initially formed ammoniophosphane complexes defied isolation, or even detection in most cases, lies in their great tendency to undergo cleavage of the P–N bond. For the preparation of stable ammoniophosphane complexes large anions with negligible nucleophilicity should therefore be used. Furthermore, we expected an additional stabilization by alkylation instead of protonation. As a consequence of these considerations, we examined the reactions of aminophosphane complexes with oxonium salts. Assuming that the stability of the desired compounds is enhanced with increasing electron density at the phosphorus atom, we started with **1**. To our surprise, we isolated **2** in very good

$$\underset{\mathbf{1}}{(CO)_5CrP(NEt_2)_3} \xrightarrow{[Me_3O][BF_4]} \underset{\mathbf{2}}{(CO)_5CrP(NEt_2)_2F} \qquad (1)$$

yield. The formation of **2** parallels most reactions with

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[1] Part 7 of the series: Exchange Reactions at Complexed Ligands of Elements of Group Vb. Part 6: Höfler, M.; Hausmann, H.; Schneider, A. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* 1978, *33B*, 1559.

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[4] Maisch, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* 1982, *37B*, 61.

[5] Febvay, J.; Casabianca, F.; Riess, J. G. *J. Am. Chem. Soc.* 1984, *106*, 7985.

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