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Synthesis and Reactivity of Methyl-Substituted Butenylmanganese Tricarbonyl Complexes Containing a Two-Electron, Three-Center Mn···H···C Interaction

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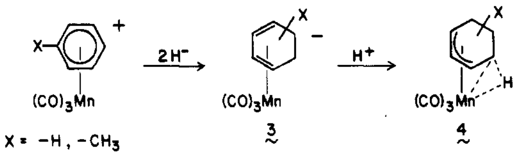
Thermolysis of (η^3-1,1-dimethylallyl)manganese tetracarbonyl, **5**, leads to CO loss and the formation of methyl-substituted butenylmanganese tricarbonyl complexes **6** and **7** characterized by an aliphatic C–H bond that is activated by metal coordination. **6** and **7** undergo two rearrangement processes which can be observed by variable-temperature ^{1}H NMR spectroscopy: (1) exchange of the three protons of the bridging methyl group ($\Delta G^{\ddagger}$ = 8.9 kcal/mol) involving a 16-electron intermediate; (2) equilibration of **6** and **7** through an 18-electron diene hydride intermediate ($\Delta G^{\ddagger}$ = 17.3 kcal/mol for **6** going to **7**). Deprotonation of **6** and **7** gives (η^4-isoprene)manganese tricarbonyl anion **8**. Methylation of **8** leads to carbon–carbon bond formation and the isolation of new compounds also characterized by the Mn···H···C interaction. Thermolysis of (η^3-*syn*-1-methylallyl)manganese tetracarbonyl and (η^3-1,1-dimethylallyl)cobalt tricarbonyl are also examined.

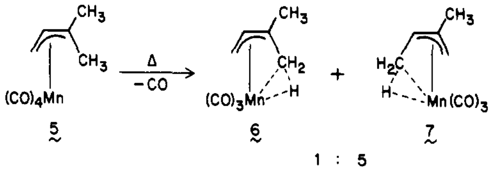
The ground-state structure of several transition-metal diene hydride complexes is not the classical structure **1** containing a terminal metal hydride bond but a bridged structure, **2**, possessing a two-electron, three-center M···H···C bond.[1–6] Such species include protonated L_3Fe(diene) and L_3Ru(diene) complexes,[3,4] Ir(η^3-$CH_2C(CH_3)C(CH_3)CH_2$-μ-H)$(PPh_3)_2H$,[5] [Mo(η^4-$C_3H_4CH_2$-μ-H)(η^4-C_4H_6)$(PMe_3)_2$]BF_4,[6] and the various substituted (cyclohexenyl)$Mn(CO)_2L$ complexes studied by us.[2,7] The dynamics and reactivity of the (cyclohexenyl)$Mn(CO)_3$ analogue in this latter series of compounds have been thoroughly examined. Neutron[8] and X-ray diffraction[2b] studies have shown an elongated carbon–hydrogen bond (C–H = 1.19 Å) and a close interaction of both the hydrogen and carbon with the metal (Mn–H = 1.84 Å; Mn–C = 2.34 Å) establishing this bridged interaction as a three-center, two-electron bond.

1 **2**

Virtually all preparations of bridged species such as **2** involve initial synthesis of the diene complex followed by protonation (Scheme I). Acyclic analogues of the diene anion **3** and the bridged complex **4** are unknown. Using a different approach to the generation of acyclic analogues of **4**, we report that thermolysis of (η^3-1,1-dimethylallyl)$Mn(CO)_4$, **5**, leads to CO loss and formation of bridged species **6** and **7** in high yields (eq 1). In addition to the synthesis of **6** and **7**, we describe (a) their dynamic rearrangements, (b) the conversion of **6** and **7** to the (η^4-isoprene)$Mn(CO)_3$ anion **8**, and (c) the reactions of diene anion **8**, with electrophilic reagents.

Scheme I. Synthesis of Cyclic Bridging Hydrides via the Double Hydride Reduction of (Arene)manganese Complexes





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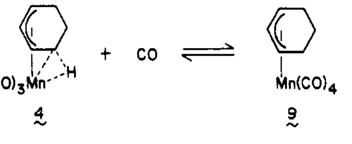
Results and Discussion

Thermolysis of (η^3-1,1-Dimethylallyl)$Mn(CO)_4$, 5. In bridged cyclohexenyl complex **4** the endo C–H σ bond can be regarded as a two-electron donor ligand to the unsaturated metal center. This two-electron "ligand" is displaced by other two-electron donor ligands such as phosphines and phosphites to generate (cyclohexenyl)$Mn(CO)_3L$ complexes.[2c,7] Remarkably, when L is CO, an equilibrium is established (eq 2). Under 1 atm of CO, **4** is favored (K_{eq} = 0.43).[2c] The (cyclohexenyl)$Mn(CO)_3L$ complexes (where L = phosphine or phosphite) lose CO either thermally or photochemically to give substituted bridged compounds (eq 3).[7] In these reactions the



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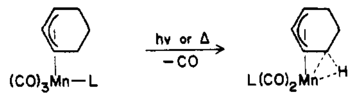

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[2] (a) Lamanna, W.; Brookhart, M. *J. Am. Chem. Soc.* **1983**, *10*, 989. (b) Brookhart, M.; Lamanna, W.; Humphrey, M. B. *Ibid.* **1982**, *104*, 2117. (c) Brookhart, M.; Lamanna, W.; Pinhas, A. R. *Organometallics* **1983**, *2*, 636. (d) Brookhart, M.; Lukacs, A. *Ibid.* **1983**, *2*, 649.

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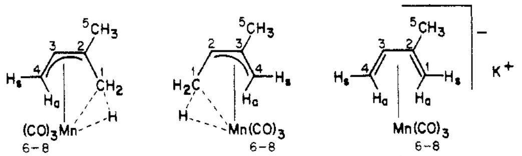
Table I. NMR Data for 6, 7, and 8



		6	7	8
$^1H^b$	1b			na
	1a	−4.2 (s)[a,c,e]	−4.4 (d, 6.5)[c,e]	−0.8 (s)[d]
	1s			0.9 (s)
	2	na	5.1 (s)	na
	3	5.1 (m)	na	4.4 (m)
	4a	−0.1 (d, 8.6)	0.1 (d, 0.2)	−1.3 (d, 7.0)
	4s	2.3 (d, 6.1)	2.4 (m)	0.6 (d, 4.0)
	5	2.5 (s)	2.0 (s)	2.0 (s)
$^{13}C^f$	1	0.5 (dt)[c,g]	−4.7 (dt, 89, 139)[c,g]	31.4 (t, 153)[d,h,j]
	2	85.4 (s)	66.1 (d, 177)	94.9 (s)
	3	95.2 (d, 163)	111.5 (s)	78.6 (d, 162)
	4	*i*	45.6 (t, 157)	38.5 (t, 152)[j]
	5	*i*	23.1 (q, 129)	25.5 (q, 126)
	6–8	*i*	225.9, 224.6, 217.9	239.3, 233.6

[a] Format: chemical shift (ppm) (multiplicity, coupling constant (Hz)). [b] 250 MHz, 25 °C. [c] CD_2Cl_2. [d] THF-d_8. [e] At ambient temperatures $H_{1b,a,s}$ appear as a single resonance. At −100 °C for 7 three one-proton signals are observed at δ −12.0, −1.4, and 0.4 for H_{1b}, H_{1a}, and H_{1s}, respectively. The signals H_{1b} and H_{1a} of 6 are observed as shoulders to the respective peaks of 7 at δ −11.8 and −1.3. Overlap problems preclude observing H_{1s} of 6. [f] 62.9 MHz. [g] −90 °C. [h] 0 °C. [i] Obscured by major isomer 7. [j] Reference 13.

methylene hydrogen which becomes bridged is part of the methylene group which is anti to the proton on the central carbon of the allyl moiety. These observations suggested that an acyclic (allyl)Mn(CO)$_4$ complex with an anti methyl group may also lose CO to generate an *acyclic* bridged complex. Indeed, heating 5 in refluxing toluene overnight under an argon stream leads to a color change from yellow to orange and loss of CO as evidenced by a tricarbonyl pattern in the CO stretching region of the IR (2020, 1945, and 1935 cm^{-1} (hexanes)). Consistent with the formation of 6 and 7 (eq 1, 93% yield) are the NMR data (Table I) and satisfactory elemental analysis.

Dynamic NMR Studies. The most characteristic feature in the ^1H NMR of both bridged compounds 6 and 7 is a high field signal for the protons of the bridging methyl groups. The signal for the major isomer 7 occurs as a doublet at δ −4.40 while that for 6 appears as a singlet at δ −4.24 (see Table I). The presence of a single resonance indicates the methyl protons exchange rapidly at 25 °C. The observed signal represents the average of the chemical shifts of H_b, H_a, and H_s (see Figure 1). At −100 °C the static spectrum can be observed and H_b, H_a, and H_s occur as three distinct one-proton signals; the chemical shifts of the remaining signals are unchanged. Assignments for the major isomer 7 are shown in Figure 1.[9a] To account for this dynamic behavior a 16-electron methyl-π-allyl intermediate, 10, is proposed which allows free rotation of the methyl group (Figure 1).[9b] A free energy of activation of 8.9 kcal/mol was determined from line-shape analysis and quantitative spin-inversion transfer (SIT) experiments (Table II).[10,11] This averaging process is analogous to an exchange process observed for the (cyclohexenyl)Mn(CO)$_3$ bridged system. Exchange between the two endo protons adjacent to the allyl moiety in 4 is also proposed to involve a 16-electron intermediate with a comparable free energy of activation (Figure 1).

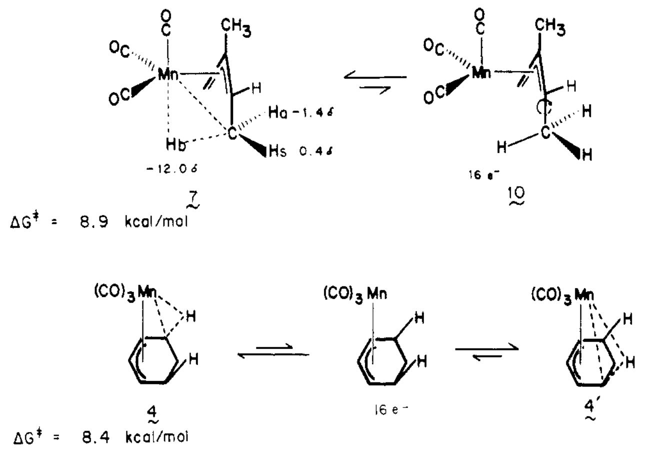


Figure 1. Comparison of exchange processes in acyclic and cyclic bridging hydrides involving an unsaturated π-allyl intermediate.

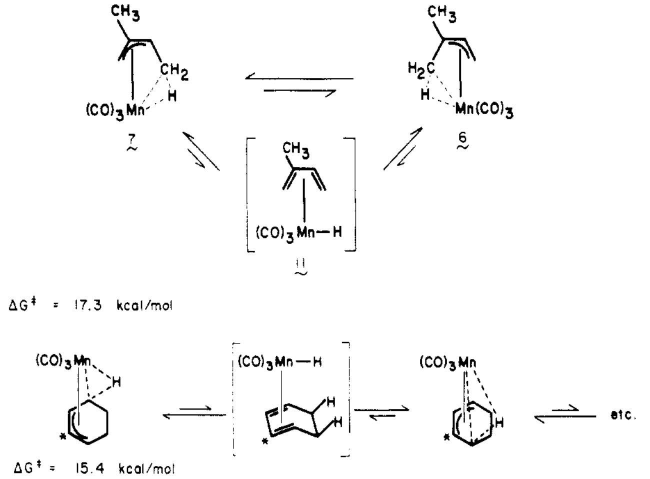


Figure 2. Comparison of exchange processes in acyclic and cyclic bridging hydrides involving an intermediate η^4-diene hydride complex.

The bridging isomers 6 and 7 are in dynamic equilibrium (see below) and are therefore inseparable. This interconversion is presumed to involve the diene hydride intermediate 11. Cleavage of the bridged carbon–hydrogen bond and transfer of hydrogen to manganese in either isomer leads to the *same* intermediate diene hydride 11 (Figure 2). The equilibrium is nondegenerate; the major isomer 7 possesses a methyl group at the central carbon of the π-allyl unit, while the minor isomer has the methyl substituent at a terminal carbon of the π-allyl unit. This methyl group site preference in 6 $\rightleftharpoons$ 7 is consistent with thermodynamic isomer ratios previously noted for (methylcyclohexenyl)Mn(CO)$_3$ derivatives[2d] (4, X = CH$_3$, Scheme I).

The equilibration of 6 and 7 can be observed at high temperatures in the ^1H NMR spectrum. In toluene-d_8 above 50 °C line broadening occurs for both isomers but even at 110 °C coalescence is not achieved. Further confirmation of interconversion and rate measurements come

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(9) (a) Signals for H_b and H_a of minor isomer 6 are seen as shoulders on these peaks for 7 (Table I). Overlap problems preclude observing H_s of 6 at −100 °C. (b) Alternatively, scrambling could proceed via rotation of the "coordinated" methyl group in such a manner as to always maintain an Mn···H···C interaction(s). Our results cannot distinguish between scrambling via a "free" methyl group and rotation of a coordinated methyl group.

(10) Dahlquist, F. W.; Longmuir, K. J.; DuVernet, R. B. *J. Magn. Reson.* **1975**, *17*, 406.

(11) Spin inversion transfer experiments (SIT) were carried out by inverting the bridging hydrogen (H_b) with a 180° pulse at −95 °C. The loss of spin label (through exchange with H_a and H_s and by spin–lattice relaxation) was measured for 13 values of τ (from τ = 0.0050–0.5000 s) where τ is the delay time.

Table II. Rate Constants and Free Energies of Activation for Exchange Processes

process	signal used	solvent	t, °C	k, s^{-1}	$\Delta G^{\ddagger}$, kcal/mol	method
bridging methyl in **7** rotation	H_{1b}	toluene-d_8	−80	306	8.9	slow exchange approx
	H_{1b}	CD_2Cl_2	−80	302	8.9	slow exchange approx
	H_{1a}	CD_2cl_2	−80	352	8.9	slow exchange approx
	$H_{1b,a,s}$	CD_2Cl_2	−95	35	9.0	SIT[a]
6 → **7**	H_{4a}	toluene-d_8	80	127	17.4	slow exchange approx
	H_1; $H_{4a,4s}$	CD_2Cl	35	3.9	17.3	SIT[b]
19s → **18**	H_{1s}	toluene-d_8	15	3.3	16.1	SST[c]
	H_{4a}	toluene-d_8	15	3.0	16.2	SST
	H_{4a}	toluene-d_8	4	0.9	16.3	SST

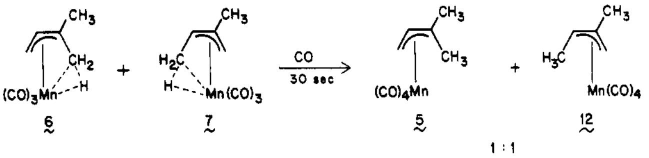
[a] Reference 11. [b] Reference 12. [c] Reference 17.

from SIT experiments, $\Delta G^{\ddagger} = 17.3$ kcal/mol, **6** → **7** (Table II).[12] Again, an analogous process involving carbon–hydrogen bond cleavage is observed in the (cyclohexenyl)$Mn(CO)_3$ bridged system with $\Delta G^{\ddagger} = 15.4$ kcal/mol (Figure 2).

Isoelectronic to bridged compounds **6** and **7** are the products obtained from protonation of the neutral (η^4-isoprene)$Fe(P(OMe)_3)_3$ reported by Ittel.[3a] Interestingly, only the isomer corresponding to **6** is observed by NMR. This compounds was not sufficiently stable above room temperature to probe the higher energy diene hydride rearrangement process.

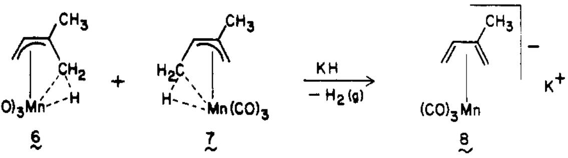
^{13}C NMR results completely confirm conclusions based on the ^1H NMR studies. The bridging carbon typically resonates at high fields (δ −4.7; Table I), which is indicative of interaction with the metal center. At room temperature (or at temperatures above coalescense for the low-energy process) the bridging carbon of **7** appears as a quartet (J_{CH} = 124 Hz). Cooling to −95 °C results in splitting of this quartet into a doublet of triplets. The 89-Hz doublet is due to coupling with the bridged hydrogen in the static structure. The low value for this coupling indicates the reduced bond order and is a result of the three-center, two-electron interaction. Such low J_{CH} values are diagnostic of M···H···C bridging systems.[1] The triplet is due to coupling to the unbridged protons on this carbon. The magnitude of this coupling (139 Hz) is larger than that expected for sp^3 carbon–hydrogen coupling constants (120–130 Hz) and approaches the value of an sp^2 carbon–hydrogen bond. This is consistent with the ground-state structure of this bridging compound being intermediate between the 16-electron allyl and a diene hydride.

Reaction with CO. The bound carbon–hydrogen bond in **6** and **7** is readily displaced by other two-electron donor ligands. Reaction of **6** and **7** with CO gas produces a rapid color change from orange to yellow. The respective π-allyl tetracarbonyls **5** and **12** are produced quantitatively (eq 4). Tetracarbonyl complexes **5** and **12** do not equilibrate at 25 °C, and thus the 1:1 ratio produced from a 5:1 ratio of 7:6 indicates more rapid trapping of **6** than of **7** by CO.



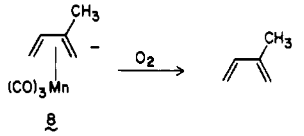
(4)

Generation and Reaction of Diene Anion 8. Another manifestation of the Mn···H···C interaction is that the bridging hydrogen is rendered acidic. Treating **6** and **7** with KH results in the formation of gas and a concomitant change in the CO stretching frequencies to lower energies (1940, 1845, and 1790 cm^{-1}), consistent with the formation of an anion. The product was identified by ^1H and ^{13}C NMR as the (η^4-isoprene)$Mn(CO)_3$ anion **8** (eq 5, Table I).[13] Acyclic manganese diene anions such as **8** are isoelectronic with the neutral (diene)$Fe(CO)_3$ complexes. While these latter compounds have been known for over 50 years,[14] the manganese analogues have been previously unreported.



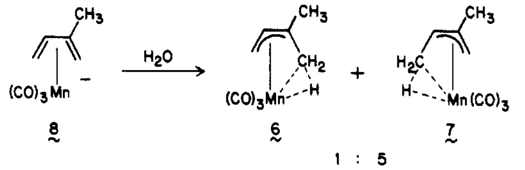
(5)

Treatment of **8** with O_2 results in oxidative cleavage of the organic moiety from the metal (eq 6). Isoprene can be isolated in good yields (76%).



(6)

Reaction of Diene Anion 8 with Electrophilic Reagents. (Diene)$Mn(CO)_3$ anions are isoelectronic to the $Mn(CO)_5$ anion and are thus expected to be basic and nucleophilic. Protonation of **8** leads to the regeneration of **6** and **7** in good yields and in the same ratio (eq 7).



(7)

Alkylation of **8** with methyl iodide rather than giving a metal alkyl results in carbon–carbon bond formation to give a complex mixture of new bridging hydrides **16**, **17**, **18**, and **19** (Scheme II). The reaction can most simply be envisioned as proceeding via the manganese alkyl complex **13** although we have no definite proof for its formation. Migration of the manganese-bound methyl group (marked by $^*CH_3$ for clarity) to C_1 yields π-allyl complex **14** which upon C–H coordination gives **16n** and **16x**. Complexes **16n** and **16x** can rearrange to **17a** and **17s** via the diene–hydride mechanism (vide supra). Consistent with methyl group site preferences previously established (see above and ref 2d) the **16** $\rightleftharpoons$ **17** equilibrium favors **17**; no **16** (<5%)

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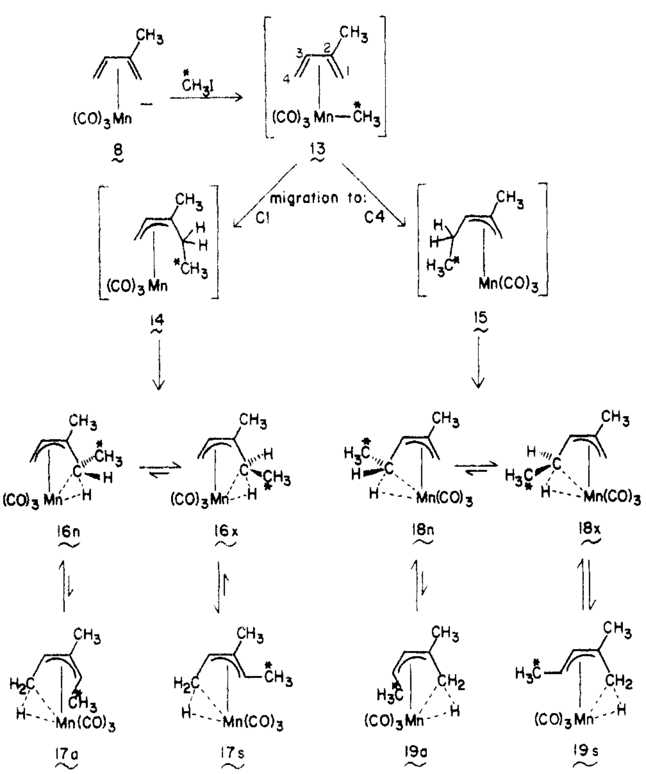
[12] SIT's were carried out by inverting the high field signals of **6** and **7** at 35 °C. Analysis of the time course for the equilibration of excess magnetization to sites H_{4a} and H_{4s} of both **6** and **7** for 15 values of τ (τ = 0.0050–5.0000 s) was used to determine the rate constant for exchange.

[13] Assignments for C_1 and C_4 are based on these assignments in (η^4-C_5H_8)$Fe(CO)_3$: Pearson, A. J. *Aust. J. Chem.* **1976**, *29*, 1679.

[14] Deeming, A. J. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 4, p 426.

Scheme II. Isomeric Products from Methylation of $[(\eta^4\text{-Isoprene})Mn(CO)_3]^-$, 8



(a) Abbreviations: suffixes n and x indicate the position of the migrated methyl group (*) when it resides on the bridging carbon, endo or exo to the allyl unit, respectively. Suffixes a and s indicate the position of the migrated methyl group (*) when it resides on a terminal carbon of the allyl moiety, anti or syn to the proton on the central carbon of the allyl, respectively.

is detected. Migration of $^*CH_3$ to C_4 yields initially **15** which upon C–H bridging gives **18n** and **18x**. Complexes **18n** and **18x** equilibrate with **19a** and **19s** via the diene–hydride mechanism. Again consistent with methyl group site preferences, significant amounts of both **18** and **19** are present at equilibrium. The ratio of (**18** + **19**)/**17** establishes a 7:1 preference for methyl migration to C_4.

The upfield ^1H region (δ −2 to −13) clearly establishes isomer ratios and these assignments.[15] Bridging methyl groups in which all three hydrogens interconvert rapidly in a degenerate equilibrium appear at the typical values of ca. δ −5 (in aromatic solvents) with slight differences for **19s** (δ −5.0) and **17s** (δ −5.2) (see Figure 3). An interesting and analytically quite useful phenomenon is seen in the ^1H NMR of **18**. Complex **18** may exist as two rapidly interconverting isomers **18x** and **18n** via ethyl group rotation. Unlike methyl rotation in **17s** and **19s**, the equilibrium is nondegenerate. The chemical shift of H_s will be the weighted average of the shift in **18x** (ca. δ −13) and **18n** (ca. δ +1.0), likewise $\delta(H_a)$ will be the weighted average in **18x** (δ −2.9) and **18n** (δ −13).[16] Thus H_s and H_a will appear as two distinct bands centered around ca. δ −7.5 [δ −13 + [δ(−2.9 + 1.0)/2]/2]. Their separation will be a quantitative measure of the ratio of the two isomers. As can be seen in Figure 3 these bands appear at δ −2.1 and

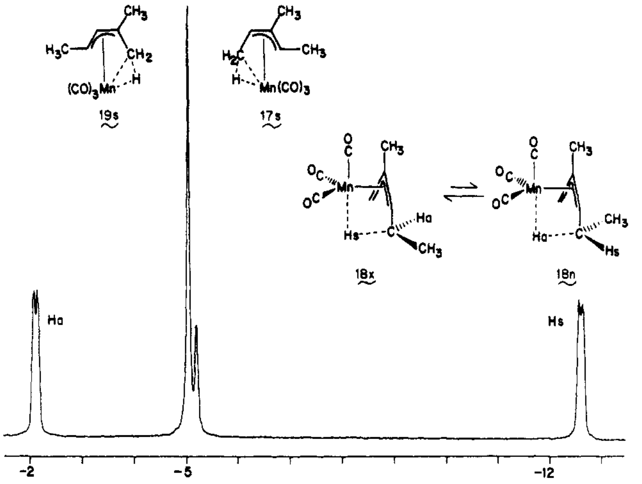


Figure 3. Room-temperature 250-MHz ^1H NMR spectrum of the products resulting from methylation of $(\eta^4\text{-}C_5H_8)Mn(CO)_3]^-$, 8, in toluene-$d_8$.

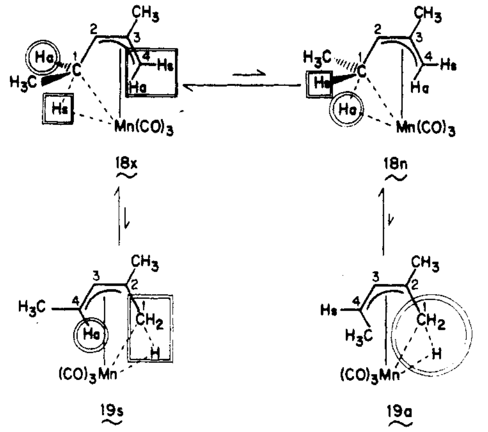


Figure 4. Hydrogen scrambling processes in **18x**, **18n**, **19s**, and **19a**. Boxes and circles represent which protons are related via exchange processes as shown by SST experiments.

−12.6 indicating a strong preference for one isomer over the other (ca. 25:1).[17] On the basis of the assumption that the exo position for the methyl group is sterically less hindered, we feel **18x** is favored. These assignments and the interconversion of **18x** and **18n** with **19s** could be confirmed by SST (spin saturation transfer) experiments. Shown in Figure 4 are the four potential products which could arise from methyl migration to C_4 in **13** (Scheme II). Irradiation of the bridging methyl resonance δ −5.0 (**19s**) at 30 °C results in substantial saturation transfer to peaks at δ −12.6, −0.4, and 2.0 (assigned to H_{1s}, H_{1a}, and H_{4s} of **18**, respectively) with no effect on the rest of the spectrum. Rate constants for this rearrangement process were determined by quantitative SST experiments at 15 °C. An activation barrier of $\Delta G^‡ = 16.2$ kcal/mol for the conversion of **19s** to **18** was calculated.[18] With a $K_{eq} = 2.6$ this translates to an activation barrier of 16.7 kcal/mol for the reverse process. Saturation transfer was also observed by separately irradiating peaks at δ −12.6 (H_{1s}, **18x** $\rightleftharpoons$ **18n**) and −2.1 (H_{1a}, **18x** $\rightleftharpoons$ **18n**). The boxes and circles in Figure 4 summarize which protons are related as a result of the exchange processes, determined by these SST experiments.

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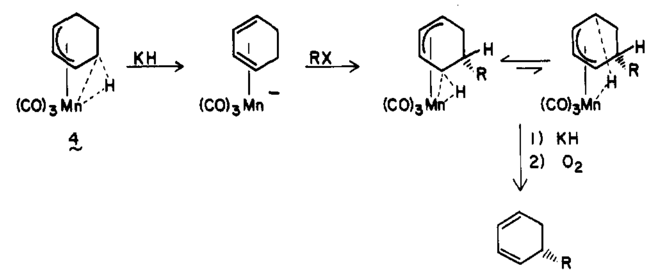
[15] Only a single isomer of both **17** and **19** are observed; these are believed to be **17s** and **19s**. The anti methyl isomers **17a** and **19a** have been discounted on steric grounds. SST experiments confirm this assumption for **19** (vide infra).

[16] The chemical shifts δ −13.0, −1.1, and −2.9 are based on the ^1H NMR of **7** in toluene-d_8 at −100 °C and are uncorrected for methyl substitution.

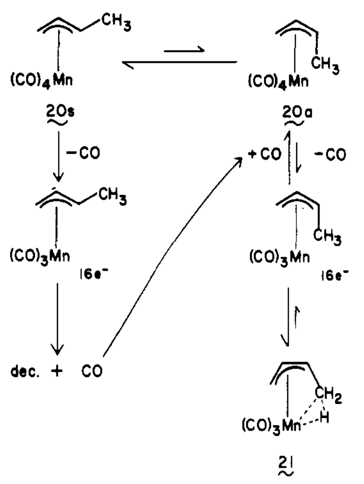
[17] This ratio is based on estimated shifts and could vary from 15:1 to quite large values. The minor isomer is certainly present in less than 8–10%.

[18] SST experiments were done at 15 and 4 °C by irradiating the signal at δ −5.05 and measuring the decrease in intensity of peaks at δ −12.5 and −0.4. (The signal at δ 2.0 was too congested to give reliable integration.)

Scheme III. Reactivity of Cyclic Bridged and Diene Anion Complexes



Scheme IV. Pathways for the Thermolysis of (η^3-1-Methylallyl)Mn(CO)$_4$, 20

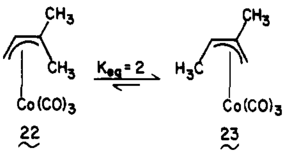


These results clearly establish that **18x** and **18n** are in equilibrium with **19s** and that H_{1a} (**18x** ⇌ **18n**) cannot exchange with H_{1s} (**18x** ⇌ **18n**). As expected irradiation of the peak at δ −2.1 (H_{1a}, **18x** ⇌ **18n**) has no effect on the bridging methyl region indicating that the anti isomer **19a** is not present in significant amounts. This conclusion was reached earlier by invoking steric arguments.

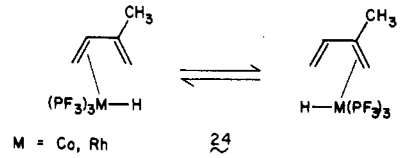
The reactions described by eq 5 through 7 and in Scheme II correspond closely to reactions observed in the (cyclohexenyl)Mn(CO)$_3$ bridging system (Scheme III).[2]

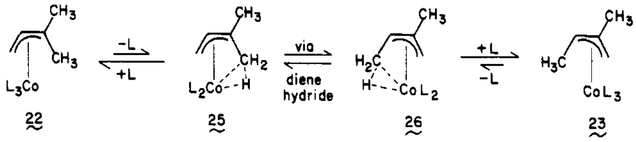
Applications to Other Systems. Attempts to synthesize the simplest analogue in this series of manganese-bridged complexes utilizing the procedure reported here have had only limited success. Heating (η^3-1-methylallyl)Mn(CO)$_4$, **20**, in refluxing toluene leads to a 20% conversion to the butenyl-bridging hydride 21 (as evidenced by a doublet in the ^{1}H NMR at δ −5.5 (C_6D_6)) with significant general decomposition. Prolonged heating (days) or higher temperatures does not improve this percentage but only leads to a poorer recovery of tractable material. The problem in the butenyl case appears to result from the low value for K_{eq} between the syn and anti forms of the tetracarbonyl 20 (Scheme IV). Loss of CO from **20a** leads to a 16-electron intermediate with a methyl group in the proper position to bridge a carbon–hydrogen bond leading to formation of 21. Loss of CO from the major syn isomer is counterproductive. The resulting 16-electron intermediate cannot stabilize itself by a bridging interaction. In refluxing toluene this intermediate likely decomposes. The liberated CO is easily scavenged by bridging hydride 21 to regenerate 20.

(η^3-1,1-Dimethylallyl)Co(CO)$_3$, **22**, has also been prepared. It is stable for days at room temperature with no change in the ^{1}H NMR. Heating for brief periods of time at 80 °C leads to the formation of the 1,2-dimethyl isomer **23** (eq 8). The equilibrium ratio is 1.3.[19] Nixon has reported a similar observation for the tris(trifluorophosphine) analogue of **22**.[20] He suggested an η^2-bound diene hydride intermediate, **24**, to account for the rearrangement. Given the results reported here, a more likely mechanism is loss of ligand (CO or PF$_3$) to form a bridging hydride intermediate, **25**, which undergoes the rearrangement through the diene hydride process (eq 9). Efforts to isolate the bridging hydrides **25** and **26** where L = CO are currently in progress.



(8)





(9)

Conclusions

An alternate synthetic route to compounds characterized by a three-center, two-electron Mn···H···C bond has been reported. This method involves ligand displacement rather than protonation of coordinated dienes. The acyclic bridging compounds reported herein are isolable and stable, as indicated by the harsh reaction conditions required for their synthesis. These compounds can be deprotonated to give an acyclic (diene)Mn(CO)$_3$ anion. The reactivity of both the acyclic bridged compounds and the diene anion is analogous to that found for the cyclohexenyl system. Dynamic NMR studies on the bridged system reveal two fluxional processes involving a lower energy 16-electron intermediate ($\Delta G^\ddagger$ = 8.9 kcal/mol) and a higher energy diene hydride intermediate ($\Delta G^\ddagger$ = 17.3 kcal/mol). Each of these rearrangement processes have analogues in the cyclohexenyl-bridged system with comparable free energies of activation ($\Delta G^\ddagger$ = 8.4 and 15.4 kcal/mol, respectively).

Finally, the stability and reactivity of the acyclic bridging compounds and the diene anion demonstrated in eq 5 through 7 and in Scheme II point to the potential for use of this type of system in the synthesis of functionalized dienes (Scheme V). Each step in Scheme V has been shown to proceed in good yields in a methyl-substituted acyclic system. Alternate synthetic routes to the parent (butenyl)Mn(CO)$_3$ bridging system to probe this synthetic utility are currently in progress.

Experimental Section

General Data. All reactions were carried out under dry, oxygen-free atmospheres using standard Schlenk techniques with

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[19] Nixon and co-workers reported *no* rearrangement of 22 to 23 when heated in benzene in a sealed tube at 60 °C, even after 24 h.[19b] The discrepancy between Nixon's observations and those reported here likely results from a combination of temperature and concentration differences.

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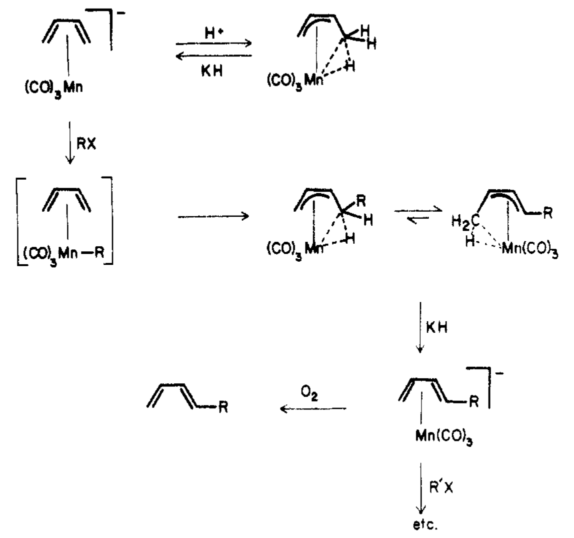
Scheme V. General Synthetic Route to Functionalized Dienes Using Bridging Hydride Compounds



a double manifold vacuum line. Nitrogen gas was purified by passage through columns of BASF catalyst R3-11 and molecular sieves (4 Å); argon was used as purchased. Hexanes and tetrahydrofuran were freshly distilled from sodium/benzophenone ketyl prior to use. Reagent grade toluene was degassed by flushing with nitrogen for ca. 20 min without further purification. Potassium hydride wash purchased 35% in mineral oil (Aldrich). KH was freed of oil by repeated washing with hexanes (3–5×). Drying in vacuo gave a free flowing powder. Dimanganese decacarbonyl and dicobalt octacarbonyl (Strem or Pressure Chemicals) and other reagents were used as purchased unless noted. Alumina used was activity III–IV and neutral unless otherwise noted. (η^3-1-Methylallyl)manganese tetracarbonyl, **20**, and (η^3-1,1-dimethylallyl)manganese tetracarbonyl, **5**, were prepared by published procedures.[21]

^{1}H NMR spectra were recorded at 250 MHz on a Bruker WM250 FT NMR spectrometer and at 100 MHz on a Varian XL-100 FT NMR spectrometer. ^{13}C NMR spectra were recorded at 62.9 MHz (Bruker WM-250). Residual solvent signals were used as internal standards for determining chemical shifts. Tetrahydrofuran-d_8 and toluene-d_8 were vacuum distilled from Na/benzophenone ketyl. Methylene-d_2 chloride and benzene-d_6 were degassed by several freeze–pump–thaw cycles. The methylene-d_2 chloride was then vacuum distilled from lithium aluminum hydride. Infrared spectra were recorded on a Beckman spectrophotometer (IR4250), and frequencies (cm^{-1}) were assigned relative to a polystyrene standard. Only bands in the carbonyl stretching region (1500–2300 cm^{-1}) were recorded. Analytical GLC analysis was obtained on a Hewlett-Packard 5750 chromatograph with a 12 ft × $^1/_8$ in., 25% QF-1 on chrom W column at 60 °C in the flame ionization detection mode.

Preparation of (η^3-C_5H_9)Mn(CO)$_3$, 6 and 7. Method A. (C_5H_9)Mn(CO)$_4$, **5** (2.70 g, 11.44 mmol), was dissolved in 190 mL of toluene in a two-necked round-bottom flask fitted with a condenser and a rubber septum. A stainless steel needle attached to an argon line was inserted through the septum below the surface of the toluene. Argon was bubbled through the solution out an oil bubbler attached to the top of the condenser. The solution was heated to reflux for 48 h, cooled, filtered through alumina (1 in. × 1 in.), and evaporated (30 °C, 25 mm) to give a dark red oil. Last traces of toluene were removed in vacuo (0.001 mm, 30 °C) to give 2.22 g of a red oil, 93% yield. Anal. Calcd $C_8H_9O_3Mn$: C, 46.18; H, 4.35; Mn, 26.40. Found: C, 46.34; H, 4.50; Mn, 26.51.

Method B. **6** and **7** could also be prepared by protonation of the isoprene anion **8**. To excess KH was added 10 mL of THF. (η^3-C_5H_9)Mn(CO)$_3$, **6** and **7** (0.45 g, 2.16 mmol), was dissolved in 30 mL of THF and the solution transferred via cannula onto the KH. Gas evolution (H_2) was observed immediately, and the solution became dark. IR indicated complete reaction. The solution of the isoprene anion was filtered through Celite (1 in. × 1 in.). One milliliter of N_2-saturated H_2O was added to the filtrate. Evaporation of the solution (30 °C, 25 mm) gave a red oil. A 40-mL sample of hexanes was added. The orange hexanes solution was dried over Na_2SO_4 and filtered through alumina (Act II, pH 10, 1 in. × 0.5 in.). Solvent removal in vacuo resulted in 0.30 g (67% yield) of **6** and **7** as verified by ^{1}H NMR.

Reaction of (η^3-C_5H_9)Mn(CO)$_3$, 6 and 7, with CO. A ^{1}H NMR sample of **6** and **7** was prepared in CD_2Cl_2. The spectrum was recorded and integrated relative to the residual solvent signal. CO was bubbled through the solution for ca. 30 s. ^{1}H NMR showed <5% **6** and **7** and near quantitative generation of tetracarbonyls **5**[19] and **12** in ca. 1:1 ratio. ^{1}H NMR (CD_2Cl_2): **12**, δ 3.7 (qd, J = 7 Hz, <1 Hz, H_1), 3.0 (dd, 2 Hz, H_{3s}), 2.2 (dd, 2 Hz, H_{3a}), 1.9 (s, CH_3), 1.4 (d, J = 6 Hz, CH_3).

Preparation of ^{1}H NMR Samples of [(η^4-C_5H_8)Mn(CO)$_3$]$^-$K$^+$, 8. An excess of KH powder was added to a 5 mm NMR tube followed by 0.5 mL of THF-d_8 and bridging hydrides **6** and **7** (ca. 50 mg). When gas evolution (H_2) ceased, the solution was degassed by three freeze–pump–thaw cycles and sealed in vacuo. Excess KH was centrifuged to the sealed end of the tube. Samples prepared this way remain stable for months.

Methylation of [(η^4-C_5H_8)Mn(CO)$_3$]$^-$K$^+$, 8. To excess KH powder was added 15 mL of THF followed by 0.68 g (3.27 mmol) of (η^3-C_5H_9)Mn(CO)$_3$, **6** and **7**, in 10 mL of THF. The solution was allowed to stir until bubbling ceased (ca. 0.5 h). The solution was filtered through Celite and concentrated in vacuo (0.001 mm) to a solid. The solid was redissolved in 20 mL of CH_2Cl_2 and 10 mL of THF. This solution was transferred to an addition funnel via cannula. The diene anion solution was added to 10 mL of neat methyl iodide (vacuum distilled from P_2O_5 immediately prior to use) over the course of 2 h during which time the mixture became cloudy (KI). The solution was filtered through alumina and evaporated to a red oil. The oil was extracted into 30 mL of hexanes and filtered. Concentration in vacuo (0.001 mm) gave 0.52 g (72% yield) of an orange oil. ^{1}H NMR (toluene-d_8): **18a** and **18n**, δ −12.6 (d, J = 9 Hz, H_{1s}), −2.1 (d, J = 9 Hz, H_{1a}), −0.4 (s, H_{4a}), 0.5 (m, CH_3), 1.7 (s, CH_3), 2.0 (H_{4s}), 4.2 (m, H_2); **19s**, δ −5.0 (s, H_1), 0.1 (m, H_{4a}), 1.1 (s, CH_3), 1.5 (d, CH_3), 4.7 (d, H_3); **17s**, δ −5.2 (d, H_1), other peaks obscured by major isomers **18x**, **18n**, and **19s**. Anal. Calcd for $C_9H_{11}O_3Mn$: C, 48.67; H, 4.99. Found: C, 48.75; H, 5.11.

Oxidative Cleavage of Isoprene from 8. To excess KH powder under 5 mL of THF was added 0.23 g (1.11 mmol) of (η^3-C_5H_9)Mn(CO)$_3$, **6** and **7**, in 10 mL of THF. After gas evolution (H_2) ceased, ca. 0.5 h, the solution was filtered through Celite. The filtrate was cooled to −70 °C, and O_2 was bubbled through the solution of ca. 10 min. A 70-μL sample of isopentane was added as a standard. Samples for analytical GLC analysis were taken from this solution. A relative response factor was determined by using a known ratio of isoprene/isopentane. Isoprene was detected in 76% yield based on **6** and **7**.

Thermolysis of (η^3-C_4H_7)Mn(CO)$_4$, 20. A 2.18-g (9.82-mmol) sample of **20** was dissolved in 200 mL of toluene. The solution was heated to reflux with a stream of argon passing through it for 16 h, cooled, filtered through alumina (1 in. × 1 in.), and evaporated (30 °C, 25 mm) to give 1.7 g of an orange oil. ^{1}H NMR in C_6D_6 indicated the material to be **20** and **21** in a ratio of 4.5:1.

Preparation of (η^3-C_5H_9)Co(CO)$_3$, 22. The method of Alper et al. was used.[22] A 11.6-g sample of NaOH in 60 mL of water was added to 0.67 g (2.92 mmol) of benzyltriethylammonium chloride. In a separate Schlenk vessel 1.0 g (2.9 mmol) of $Co_2(CO)_8$ and 0.68 mL (5.85 mmol) of 1-bromo-3-methyl-2-butene were added to 60 mL of benzene. This red mixture was cannula transferred to the water solution. The solution was stirred vigorously at room temperature. When gas evolution (CO) ceased (ca. 2 h), the benzene layer had become clear orange. The solution was decanted from the water via cannula, evaporated (30 °C, 25 mm) to a red oil, redissolved in 35 mL of hexanes, dried over Mg_2SO_4, filtered, and concentrated in vacuo to yield 0.68 g (55% based on $Co_2(CO)_8$) of oil: IR ν_{CO} (hexanes) 1990, 2045 cm^{-1}; ^{1}H NMR (toluene-d_8) δ 4.3 (dd, J = 11 Hz, 7 Hz, H_2), 2.8 (dd, J =

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7 Hz, 1 Hz, H_{3s}), 2.2 (dd, $J = 11$, 1 Hz, H_{3a}), 1.4 (s, CH_3), 1.0 (s, CH_3).

Thermolysis of (η^3-C_5H_9)$Co(CO)_3$, 22, in a Sealed Tube. **22** was taken up in 0.5 mL of toluene-d_8 and sealed in vacuo (0.001 mm). ^1H NMR showed the sample remains unchanged for days at room temperature. The tube was heated to 80 °C for 10 min. ^1H NMR indicated **23** had grown in clearly at the expense of **22** (residual solvent signal used as a standard) in a 1:1 ratio. Prolonged heating established $K_{eq} = 1.3$ at 60 °C. **23**: ^1H NMR (toluene-d_8) δ 3.9 (qd, $J = 7$, 2 Hz, H_1), 3.05 (d, $J = 2$ Hz, H_{3s}), 2.6 (m, H_{3a}), 1.4 (s, CH_3), 0.9 (d, $J = 7$ Hz, CH_3).

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Carbonyl Insertion Reactions. 1. Structure and Formation of $(HFe(CO)_4)^-$, $((CO)_3FeCHO)^-$, and $((CO)_4FeCHO)^-$

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Calculations within a MINDO framework have been made for $(HFe(CO)_4)^-$, $((CO)_3FeCHO)^-$, $((CO)_4FeCHO)^-$, and intermediate structures for hydride migration and CO addition. In contrast to previous speculation the bending of the equatorial CO ligands in $(HFe(CO)_4)^-$ toward the hydride ligand is found to be due to increased Fe–C bond strength in the axial CO ligand as the bending occurs. The effect of the hydride ligand on the bonding of the CO ligand and the effect of the CO ligands on the Fe–H bond are discussed. The instability of the formyl group in $((CO)_4FeCHO)^-$ is traced to the highest occupied molecular orbital being high in energy relative to other molecular orbitals, putting a large negative charge on the H atom, and being antibonding for the C–H bond. The calculated potential energy curve for the hydride migration from the Fe atom to a carbon atom indicates that the formyl complex $((CO)_3FeCHO)^-$ is 24–44 kcal/mol less stable than the metal hydride and has no stable potential well. This is in accord with the fact that this hydride migration has never been observed. Oxidation of the complex is calculated to promote the migration. Calculations for CO addition to $(HFe(CO)_4)^-$ to produce a formyl for the case of a concerted addition as the hydride migration occurs and for the case where the CO addition is a second step after the hydride has migrated to give a tetrahedral $((CO)_3FeCHO)^-$ have been made. The activation energies calculated vary from 27 to 31 kcal/mol. The activated complex occurs in all cases when the hydride ligand moved most of its way. The major factor in the activation energy is the hydride migration.

Introduction

There exists a substantial body of organometallic literature dealing with alkyl migration reactions to form acyls.[1] These reactions are important in heterogeneous and homogeneous catalysis as well as in stoichiometric organometallic synthesis. The smallest unit which might be considered to migrate is a hydrogen atom. Although many transition-metal alkyls readily migrate to an adjacent carbonyl to form an acyl, the rearrangement of a transition-metal hydride to a formyl has not been observed.[2–4] The first synthesis of a formyl complex was the synthesis of $((CO)_4FeCHO)^-$ from $Na_2Fe(CO)_4$ by Collman and Winter.[5] Subsequently, many transition-metal formyls have been reported but most have a half-life near room temperature in the range from seconds to a few days.[2] The reluctance of transition-metal hydrides to shift the hydrogen atom to a CO to give a metal formyl has not kept formyl complexes from being suggested as intermediates in the catalytic reduction of CO with H_2.[6–8] The considerable difficulty of a formyl formation step may be greatly reduced by the presence of Lewis acid electrophiles. The promotion of the alkyl migration reaction in $(RFe(CO)_4)^-$ by Na^+ is well-known.[9] Lewis acids have been shown to promote alkyl migration from metals to CO both in solution and on surfaces.[10,11] Oxidation of the metal has been found to induce alkyl migration to form an acyl.[12]

Relatively little theoretical attention has been given to transition-metal alkyl migration reactions to form acyls. Orbital usage has been looked at for some cases.[13] The stability of nickel formyl radicals (NiCHO) relative to NiH, NiCO, and other Ni species has been calculated.[14] In this paper the geometric and electronic structure of $(HFe(CO)_4)^-$ and $((CO)_4FeCHO)^-$ are examined. Calculations are

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