a deficiency of RX. As noted from Chart I, the group 8B hydrides, $HM(CO)_4^-$ (M = Fe, Ru), were less reactive than their group 6B analogues toward these H/X displacement reactions. (Only the most reactive halides (such as acid chlorides) have been reported to be reduced by $HFe(CO)_4^-$.[6]) The phosphite-substituted metal hydrides $HM(CO)_4P^-$ are more reactive toward primary alkyl halides than are their pentacarbonyl analogues. Such enhanced reactivity was anticipated as the substitution of CO by a P-donor ligand increases the partial negative charge on the hydride.[7] However, this enhanced reactivity is not observed for the branched alkyl halides. There is actually a 250-fold diminution of reactivity through the series n-C_4H_9Br, 2-C_4H_9Br,[8] and t-C_4H_9Br for cis-$HW(CO)_4P(OMe)_3^-$, resulting in a *reversal* of reactivity order for cis-$HW(CO)_4P(OMe)_3^-$ and $HW(CO)_5^-$ for reductions of tertiary centers. In fact the reduction of a mixture of t-BuBr and n-BuBr by $HW(CO)_4P(OMe)_3^-$ produces n-C_4H_{10} exclusively, whereas the same mixture of bromides yields a mixture of n-C_4H_{10} and i-C_4H_{10} with $HW(CO)_5^-$ as reductant. Such a pronounced ligand effect is expected to be very useful in developing selective transition-metal hydride transfer agents.

Several experiments of import to the mechanism of hydride transfer are under way and will be presented in the full report of this study. Two especially noteworthy results are as follows. The reaction of $HW(CO)_5^-$ with 6-bromo-1-hexene in THF solution yielded a mixture of 1-hexene and methylcyclopentane (1.6:1 ratio, 80% overall yield) whereas $HW(CO)_4P(OMe)_3^-$ produced only 1-hexene, 85% yield, under identical reaction conditions. The detection of cyclized products derived from bromoalkenes during hydride/halide displacement has been used as an indicator of radical species in reactions of the mechanistically well-characterized $CpV(CO)_3H^-$ as well as in tin hydrides.[9] By this criterion $HW(CO)_5^-$ appears to react with at least some radical character; however this test provided no positive evidence for the involvement of radicals in the case of $HW(CO)_4P(OMe)_3^-$. These hydrides, $HW(CO)_5^-$ and $HW(CO)_4P(OMe)_3^-$, reacted with exo-2-bromonorborane to yield norbornane. The $HW(CO)_5^-$ reaction requires a few hours and the phosphite hydride requires days at room temperature. When the corresponding deuterides were used the ^2H NMR of the norbornane product indicated a highly selective (exo) incorporation with $DW(CO)_5^-$, eq 3, but a mixture of exo- and endo-deuterated products for $DW(CO)_4P(OMe_3)_3^-$, eq 4.

The result of eq 3 suggests a front-side displacement with a specificity that is quite surprising in view of the 6-bromo-1-hexene study described above. The result in eq 4 implies at least some inversion at the substitution center, analogous to the similarly slow reduction of exo-2-bromonorbornane with $LiBDEt_3$ which resulted in the exclusive formation of $endo$-d isomer.[4] In that case the inversion at the substitution center was taken as evidence for an S_N2 mechanism. At this stage in our investigation we can only conclude the obvious: (1) the all-carbonyl hydride appears to have some radical character associated

(3)

(δ = 1.49)

(4)

(δ = 1.18)
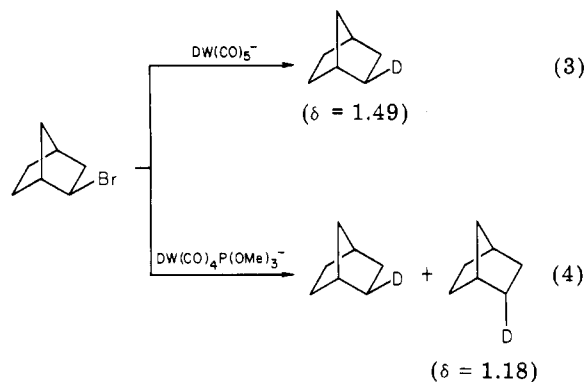
with its alkyl halide reductions; (2) the phosphite-substituted hydride may have considerable ionic character and little radical character associated with its hydride-transfer reactions; and (3) an ordered transition state is appropriate to both.[5,10]

The current status of the literature involving metal hydrides, SET processes, and stereochemistry[11] (retention, inversion, or racemization of configuration) would permit various (and lengthy) interpretations of our results. Furthermore the balance in M–H bond character leading to H· transfer, SET, or H⁻ transfer has been noted in other systems,[12] and it is not surprising that ligand effects might also alter M–H reactivity. Regardless of mechanism, the value of the above study is in the established reactivity order and in the potential development of useful hydride-transfer reagents.

(6) (a) Cole, T. E.; Pettit, R. *Tetrahedron Lett.* 1977, 781. (b) There has been a report on the dehalogenation of organic halides in an in situ generated $HFe(CO)_4^-$ which was conducted in a highly polar medium. Alper, H. *Ibid.* 1975, 2257.

(7) Richmond, T. G.; Basolo, F.; Shriver, D. F. *Organometallics* 1982, *1*, 1624.

(8) k_2 = 4.24 (±0.18) × 10⁻³ s⁻¹ M⁻¹.

(9) (a) Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* 1978, *100*, 7902. (b) Walling, C.; Cioffari, A. *Ibid.* 1972, *94*, 6059. (c) Julia, M. *Pure Appl. Chem.* 1967, *15*, 167. (d) Julia, M. *Acc. Chem. Res.* 1971, *4*, 386. (e) Lal, D.; Griller, D.; Hueband, S.; Ingold, K. U. *J. Am. Chem. Soc.* 1974, *96*, 6355. (f) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *Ibid.* 1981, *103*, 7739.

(10) The activation parameters for the reaction of cis-$HW(CO)_4P(OMe)_3^-$ and t-BuBr at 26 °C are $\Delta H^\ddagger$ (kcal/mol) = 13.3 ± 1.8 and $\Delta S^\ddagger$ (eu) = −31.4 ± 6.4. Errors calculated at 90% confidence limit.

(11) Ashby, E. C.; DePriest, R. *J. Am. Chem. Soc.* 1982, *104*, 6144 and references therein.

(12) (a) Jones, W. D.; Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* 1981, *103*, 4415. (b) Lusztyk, J.; Lusztyk, E.; Maillard, B.; Lunazzi, L.; Ingold, K. U. *Ibid.* 1983, *105*, 4475. (c) Menapace, L. W.; Kuivila, H. G. *Ibid.* 1964, *86*, 3047. (d) Ashby, E. C.; DePriest, R. N.; Pham, T. N. *Tetrahedron Lett.* 1983, 2825.

Haptotropic Rearrangements. Kinetics and Mechanism of the Rearrangement of $Mn(\eta^6$-$C_{13}H_9)(CO)_3$ to $Mn(\eta^5$-$C_{13}H_9)(CO)_3$

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Summary: The rate constants and activation parameters for the following rearrangements in hexane have been

determined: $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3 \rightarrow Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$, $Mn(\eta^6\text{-}C_{13}H_9)(CO)_2P(n\text{-}Bu)_3 \rightarrow Mn(\eta^5\text{-}C_{13}H_9)(CO)_2P(n\text{-}Bu)_3$, and $Mn(\eta^6\text{-}C_{13}H_8(t\text{-}Bu))(CO)_3 \rightarrow Mn(\eta^5\text{-}C_{13}H_8(t\text{-}Bu))(CO)_3$. Within experimental error, $\Delta H^{\ddagger}$ = 24–25 kcal/mol for all three rearrangements. These rearrangements are all intramolecular, probably going through an η^3 intermediate, as theoretically predicted. In addition, $Mn(\eta^5\text{-}C_{13}H_9)$-$(CO)_2P(n\text{-}Bu)_3$ rapidly reacts with gaseous HCl in CH_2Cl_2 to form $[Mn(\eta^6\text{-}C_{13}H_{10})(CO)_2P(n\text{-}Bu)_3]^+$. Labeling studies with DCl suggest that protonation is random, not stereospecific.

Haptotropic rearrangements, in which a metal–ligand moiety migrates from one coordination site to another on an organometallic ligand, have been the subject of both experimental[1] and theoretical[2] studies. In 1977 Treichel and Johnson[3] reported that $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$ rearranges irreversibly upon heating to $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$. Recently, Albright and co-workers[2,4] predicted the activation energy of this η^6–η^5 rearrangement to be 27–29 kcal/mol. We report here the experimental value of $\Delta H^{\ddagger}$ for this process and for two other fluorenyl manganese derivatives.

Table I gives the values of $\Delta H^{\ddagger}$ for the rearrangement of three η^6-fluorenyl complexes to η^5-fluorenyl complexes.[5] Within experimental error, all three compounds have the same $\Delta H^{\ddagger}$ which is 24–25 kcal/mol. These values are close to those predicted by Albright and co-workers of 27–29 kcal/mol and provide the first experimental support of their mechanism for the η^6–η^5 rearrangement. This mechanism is shown in Scheme I.
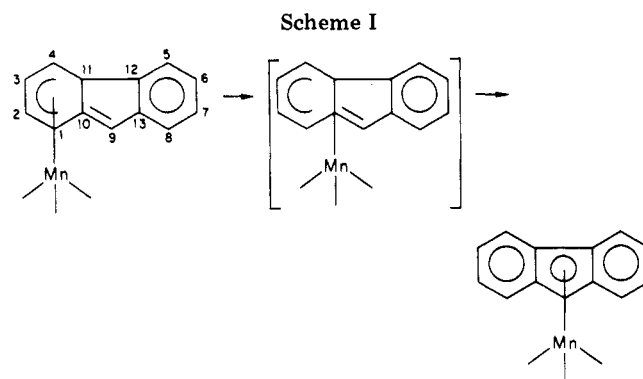
Scheme I

Scheme I suggests. However, this does not rule out the pathway, it merely shows that the $Mn(CO)_3$ moiety may not pass close enough to C(9) to be greatly hindered by the *tert*-butyl group. It should also be noted that the rearrangement is not affected by metal basicity; the more basic $Mn(CO)_2P(n\text{-}Bu)_3$ moiety has the same rearrangement activation energy as the $Mn(CO)_3$ moiety.

The mechanism of this rearrangement is clearly intramolecular. Lowering the concentration of $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$ does not affect the rate constant of the reaction, arguing against a biomolecular interchange process. The negligible $\Delta S^{\ddagger}$ also supports an intramolecular rearrangement. The rate of rearrangement of the $Cr(CO)_3$ moiety in tricarbonyl(2,3-dimethylnaphthalene)chromium was also found[6] to proceed by an intramolecular rearrangement in decane.

Table I. Rate Constants and Activation Parameters for the η^6–η^5 Rearrangement of Several Manganese Fluorenyl Compounds in Hexane

system	T, °C	k^a, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
$Mn(\eta^6\text{-}C_{13}H_9)(CO)_3 \rightarrow$	41.0	5.64×10^{-5}	25.2 ± 0.1	$+2.3 \pm 0.4$
$Mn(\eta^5\text{-}(C_{13}H_9)(CO)_3$	50.0	1.83×10^{-4}		
	60.0	6.07×10^{-4}		
$Mn(\eta^6\text{-}C_{13}H_9)(CO)_2Pn\text{-}Bu_3 \rightarrow$	40.5	8.89×10^{-5}	24.2 ± 1.4	-0.3 ± 3.6
$Mn(\eta^5\text{-}C_{13}H_9)(CO)_2Pn\text{-}Bu_3$	50.0	2.53×10^{-4}		
	60.0	9.01×10^{-4}		
$Mn(\eta^6\text{-}C_{13}H_8(t\text{-}Bu))(CO)_3 \rightarrow$	40.0	3.56×10^{-5}	24.2 ± 1.0	-1.6 ± 3.0
$Mn(\eta^5\text{-}C_{13}H_8(t\text{-}Bu))(CO)_3$	50.0	1.32×10^{-4}		
	60.5	4.16×10^{-4}		

^{a} Values are reproducible to within ±5%.

In an effort to test this mechanism, tricarbonyl(η^6-9-*tert*-butylfluorenyl)manganese was prepared[5] in order to determine if the 9-*tert*-butyl group would retard isomerization by the proposed path via C(10), instead of the ML_3 moiety moving directly across from the center of the arene to the center of the cyclopentadienyl. Although the *tert*-butyl group slightly slows down the rate of rearrangement, the effect is not as large as the η^3 pathway in

Furthermore, we have examined the chemistry of Mn-$(\eta^5\text{-}C_{13}H_9)(CO)_2P(n\text{-}Bu)_3$ in some detail. A solution of $Mn(\eta^5\text{-}C_{13}H_9)(CO)_2P(n\text{-}Bu)_3$ in CH_2Cl_2 reacts rapidly upon treatment with gaseous HCl. The IR and ^1H NMR spectra are identical with those of an independently prepared[5] sample of $[Mn(\eta^6\text{-}C_{13}H_{10})(CO)_2P(n\text{-}Bu)_3]^+$. This is in contrast to $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ which does not react with HCl under these conditions,[3] but it has recently been reported[7] to react with CF_3COOH after extended periods of time. Carrying out the reaction in DCl indicates that the ring protonation at C(9) is nonstereospecific. Examination of the ^1H NMR of $[Mn(\eta^6\text{-}C_{13}H_9D)(CO)_2P(n\text{-}Bu)_3]^+$ indicates the presence of both the endo and exo deuterium isomers. For bis(indenyl)iron,[8] protonation is stereospecific in the endo position, probably through initial iron protonation. This is apparently not the case here. Although substitution of CO by P(n-Bu)$_3$ makes the metal more basic and therefore more susceptible to protonation, C(9)

(1) (a) Nicholas, K. M.; Kerber, R. C.; Steifel, E. I. *Inorg. Chem.* **1971**, *10*, 1519. (b) Johnson, J. W.; Treichel, P. M. *J. Am. Chem. Soc.* **1977**, *99*, 1427. (c) Thoma, T.; Pleshakov, V. G.; Prostakov, N. S.; Ustynyuk, Yu. A.; Nesmeyanov, A. N.; Ustynyuk, N. A. *J. Organomet. Chem.* **1980**, *192*, 359. (d) Nesmeyanov, A. N.; Ustynyuk, N. A.; Thoma, T.; Protakov, N. S.; Soldantenkov, A. T.; Pleshakov, V. G.; Urga, K.; Ustynyuk, Yu. A.; Trifonova, O. J.; Oprunenko, Yu. F. *Ibid.* **1982**, *231*, 5. (e) Cunningham, S. D.; Öfele, K.; Willeford, B. R. *J. Am. Chem. Soc.* **1983**, *105*, 3724.

(2) Albright, T. A.; Hofmann, P.; Hoffmann, R.; Lillya, P.; Dobosh, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 3396.

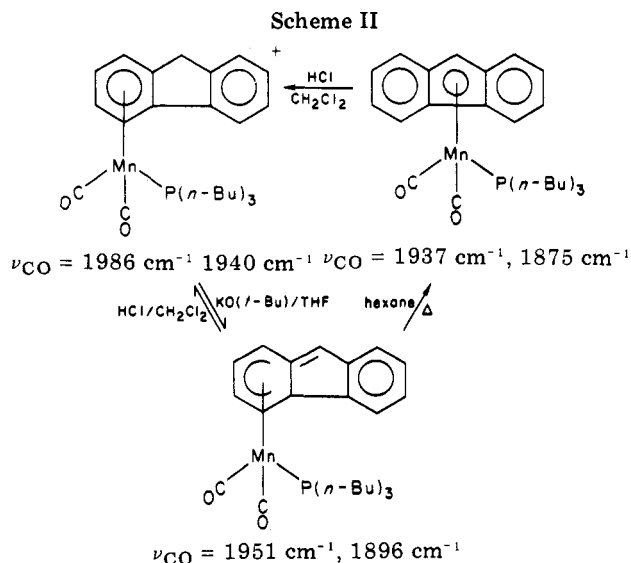(3) Treichel, P. M.; Johnson, J. W. *Inorg. Chem.* **1977**, *16*, 749.

(4) Albright, T. A., personal communication.

(5) The new compounds [Mn(η^6-C$_{13}$H$_{10}$)(CO)$_2$P(n-Bu$_3$)]PF$_6$, Mn(η^5-C$_{13}$H$_9$)(CO)$_2$P(n-Bu)$_3$, [Mn(η^6-C$_{13}$H$_8$(t-Bu))(CO)$_3$]PF$_6$, and Mn(η^5-C$_{13}$H$_8$(t-Bu))(CO)$_3$ were prepared by the method of Treichel and Johnson.[3] All have been characterized by elemental analysis and ^1H and ^{13}C NMR. The ^1H and ^{13}C NMR are very similar to the parent spectra reported in ref 3.

(6) Deubzer, B.; Fritz, H. P.; Kreiter, C. G.; Öfele, K. *J. Organomet. Chem.* **1967**, *7*, 289 and as reported in ref 2.

(7) Yezernitskaya, M. G.; Lokshin, B. V.; Zoloanovich, V. I.; Lobanova, I. A.; Kolobova, N. E. *J. Organomet. Chem.* **1982**, *234*, 329.

(8) Treichel, P. M.; Johnson, J. W. *J. Organomet. Chem.* **1975**, *88*, 207.

Scheme II

ν_{CO} = 1986 cm^{-1} 1940 cm^{-1} ν_{CO} = 1937 cm^{-1}, 1875 cm^{-1}

ν_{CO} = 1951 cm^{-1}, 1896 cm^{-1}

also has a greater amount of negative charge, and protonation may take place directly on C(9). Further support of this assertion comes from the fact that a strong base like potassium *tert*-butoxide is needed to deprotonate [Mn-(η^6-C$_{13}$H$_{10}$)(CO)$_2$P(n-Bu)$_3$]$^+$, whereas bases as weak as triethylamine will deprotonate[3] [Mn(η^6-C$_{13}$H$_{10}$)(CO)$_3$]$^+$. Measurements of the pK_a of these compounds are currently in progress. These reactions are summarized in Scheme II.

The cyclohexadienyl representation of Mn(η^6-C$_{13}$H$_9$)-(CO)$_2$P(n-Bu)$_3$ is in accord with the recently determined[9] structure of Mn(η^6-C$_{13}$H$_9$)(CO)$_3$. This suggests that hexadienyl–arene bonding may be necessary to permit the η^6–η^5 rearrangement, since Fe(η^6-C$_{13}$H$_9$)(η^5-C$_5$H$_5$)[1b] does not undergo the η^6–η^5 rearrangement, and it has been shown to have a delocalized-arene-bonded iron with the negative charge localized at C(9) by both its structure and its chemistry.

In conclusion, our experimental studies on the haptotropic rearrangements of some manganese fluorenyl compounds support the theoretical values of the activation energy and the predicted pathway for these rearrangements.

(9) Treichel, P. M.; Fivizani, K. P.; Haller, K. J. *Organometallics* **1982**, *1*, 931.

arylphosphine (PPh$_3$ or P(p-MeC$_6$H$_4$)$_3$, linked to PPh$_2$-functionalized polystyrene or PPh$_2$-functionalized (aryloxy)phosphazenes) has revealed a time-dependent decrease in catalytic activity due to a cobalt-mediated phosphorus–carbon bond cleavage. Benzene and benzyl alcohol were detected as the cleavage products. When olefin is omitted from the reaction, R$_2$PH is formed. The detection of p-MeC$_6$H$_4$CH$_2$OH indicates that oxidative addition of the P–aryl bond to Co is at least a partial contribution to the process. These results are relevant to transition-metal–triarylphosphine catalysis in general and put a new perspective on "immobilized" homogeneous catalysis.

The use of phosphine-modified cobalt carbonyl hydroformylation catalysts has been an industrially practiced process for many years.[1] We have recently obtained evidence that cobalt-mediated phosphorus–carbon bond cleavage[2] is responsible for the steady decrease in catalytic activity observed in homogeneous and "immobilized" cobalt carbonyl/triarylphosphine hydroformylation systems.

Triarylphosphines are frequently used as ligands in transition-metal-catalyzed reactions,[3] and it has been assumed that their carbon–phosphorus bonds are chemically inert under the reaction conditions employed.[4] In addition, arylphosphine functionality has been the ligand of choice through which metal fragments have been covalently bonded to a variety of organic and inorganic polymers in order to "immobilize" them.[4,5] Although previous researchers[6] have concerned themselves with metal-phosphorus dissociation, which results in metal loss under industrial flow conditions, we are not aware of any studies that have dealt with cleavage of the ligating groups from the immobilization carrier. Such a situation, if present, would obviously create serious problems.

We have identified phosphorus–carbon bond cleavage as a mode of catalyst deactivation during a study of 1-hexene hydroformlyation reactions catalyzed by triarylphosphine-substituted cobalt carbonyl species, Co$_2$-(CO)$_8$/8PR$_3$, where the PR$_3$ ligands examined have included triphenylphosphine, tri-p-tolylphosphine, tribenzylphosphine, diphenylphosphine-functionalized polystyrene (1), a ((diphenylphosphino)phenoxy)poly-((aryloxy)phosphazene) (2), and a phosphazene model analogue (3).[7]

Polymers 1 and 2 and trimer 3 were examined as functionalized supports for cobalt catalyst systems in a con-

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(2) P–C bond cleavage has been observed previously, but not directly, in catalytic reactions. See: Kikukawa, K.; Yamane, T.; Takagi, M.; Matsuda, T. *Bull. Chem. Soc. Jpn* **1979**, *52*, 1187. Kaneda, K.; Sano, K.; Teranishi, S. *Chem. Lett.* **1979**, *1*, 821. Nakamura, A.; Otsuka, S. *Tetrahedron Lett.* **1974**, 463. Fahey, D. R.; Mohan, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 4499. Nishiguchi, T.; Tanaka, K.; Fukuzumi, K. *J. Organomet. Chem.* **1980**, *193*, 37. Maclaughlin, S. A.; Carty, A. J.; Taylor, N. J. *Can. J. Chem.* **1982**, *60*, 88.

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(4) Bailey, D. C.; Langer, S. H. *Chem. Rev.* **1981**, *81*, 109.

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(6) For example: Lang, W. H.; Jurewicz, A. T.; Haag, W. O.; Whitehurst, D. O.; Rollman, L. D. *J. Organomet. Chem.* **1977**, *134*, 85.

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Cobalt-Mediated Phosphorus–Aryl Bond Cleavage during Hydroformylation

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Summary: Close examination of 1-hexene hydroformylation reactions catalyzed by cobalt carbonyl/tri-