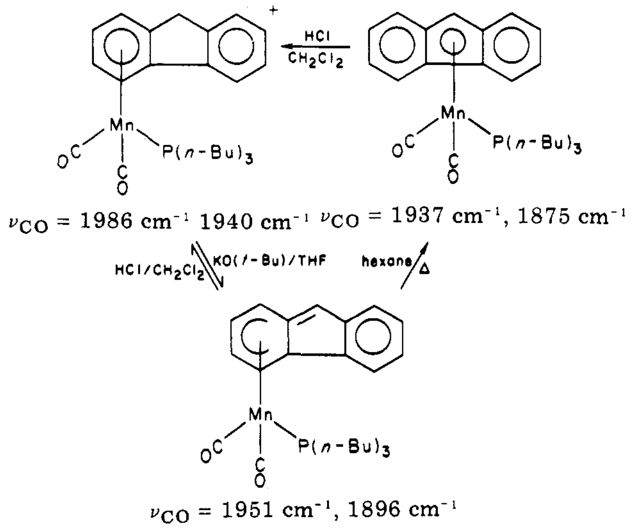
Scheme II



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 $[Mn(\eta^6\text{-}C_{13}H_{10})(CO)_2P(n\text{-}Bu)_3]^+$, whereas bases as weak as triethylamine will deprotonate[3] $[Mn(\eta^6\text{-}C_{13}H_{10})(CO)_3]^+$. Measurements of the pK_a of these compounds are currently in progress. These reactions are summarized in Scheme II.

The cyclohexadienyl representation of $Mn(\eta^6\text{-}C_{13}H_9)(CO)_2P(n\text{-}Bu)_3$ is in accord with the recently determined[9] structure of $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$. This suggests that hexadienyl–arene bonding may be necessary to permit the η^6–η^5 rearrangement, since $Fe(\eta^6\text{-}C_{13}H_9)(\eta^5\text{-}C_5H_5)$[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.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for support of this research. We are indebted to Professor Frederick G. Bordwell and his group for a sample of 9-*tert*-butylfluorene.

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

Cobalt-Mediated Phosphorus–Aryl Bond Cleavage during Hydroformylation

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Received November 15, 1983

Summary: Close examination of 1-hexene hydroformylation reactions catalyzed by cobalt carbonyl/triarylphosphine (PPh_3 or $P(p\text{-}MeC_6H_4)_3$, 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_2PH is formed. The detection of $p\text{-}MeC_6H_4CH_2OH$ 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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[1] See: Slaugh, L. H.; Mullineaux, R. D. *J. Organomet. Chem.* 1968, *13*, 469. Paulik, F. E. *Catal. Rev.* 1972, *6*, 49. Tucci, E. R. *Ind. Eng. Chem. Prod. Res. Develop.* 1970, *9*, 516; 1968, *7*, 125.

[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.

[3] Heck, R. F. "Organotransition Metal Chemistry"; Academic Press: New York, 1974. Parshall, G. W. "Homogeneous Catalysis"; Wiley-Interscience: New York, 1980.

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

[5] Hodge, P.; Sherrington, D. C. "Polymer Supported Reactions in Organic Synthesis"; Wiley-Interscience: New York, 1980.

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

[7] Details on the preparation of the polyorganophosphazenes have been given elsewhere. See: Allcock, H. R.; Evans, T. L.; Fuller, T. J. *Inorg. Chem.* 1980, *19*, 1026. Allcock, H. R.; Evans, T. L.; Fuller, T. J. *Macromolecules* 1980, *13*, 1325. All cock, H. R.; Lavin, K. D.; Tollefson, N. M.; Evans, T. L. *Organometallics* 1983, *2*, 267.

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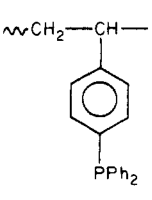
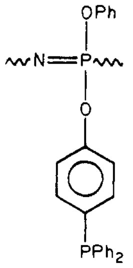
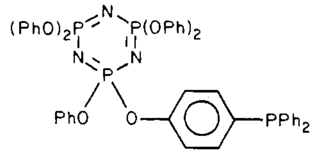


1



2

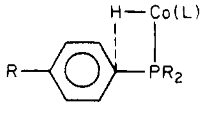


3

tinuation of our studies in the area of polymer-supported hydroformylation catalyst systems.[8] We find that the cobalt catalysts derived from 1, 2, and 3 lose catalytic activity with time, due both to loss of cobalt and loss of tertiary phosphine functionality. Thus exposure of $Co_2(CO)_8$ bound to 1, 2, or 3 to hydroformylation conditions (190 °C; heptane or toluene solvent; 2000 psig of 1:1 CO/H_2) resulted in substantial loss of phosphine functionality (microanalysis of the used catalyst revealed 15–25% loss of P in 28 h for 1 and 30% loss of P in 48 h for 2; ^{31}P NMR revealed 50% loss of pendant phosphorus from 3 in 48 h). In addition, the catalyst derived from 1 yielded $^1/_2$ mol of benzene per mol of cobalt after 48 h.

In an analogous fashion GC analysis of hydroformylation reaction mixtures with or without 1-hexene substrate, catalyzed by the homogeneous systems $Co_2(CO)_8/8PR_3$ (R = Ph, CH_2Ph), also revealed a release of benzene or toluene.[9] If the reactions are carried out without the 1-hexene substrate, diarylphosphine, R_2PH (R = Ph, p-MeC_6H_4, CH_2Ph), can be detected by ^{31}P NMR.[10,11] We believe that this represents the first direct detection of R_2PH generated by a PPh_3-ligated catalyst system.

Several possible intermediates (4, 5, 6) can be proposed for the metal-catalyzed P–C bond cleavage. Three possibilities seem plausible: (1) simple electrophilic substitution via an intermediate such as 4, (2) "oxidative addition" of the phosphorus–aryl bond via an intermediate such as 5, or (3) o-metalation and subsequent hydrogenolysis of an intermediate such as 6.[12] The production of benzene or toluene does not distinguish between these three possibilities; however, close examination of a hydroformylation reaction catalyzed by $Co_2(CO)_8/8P(p\text{-}MeC_6H_4)_3$ revealed the formation of p-methylbenzyl alcohol[13] but no m-methyl product. We feel that an oxidative-addition mechanism could be operative for these reactions in which para-specific CO insertion occurs. Whether a cobalt–phenyl intermediate is responsible for the production of benzene or toluene is at this point unknown.[12]



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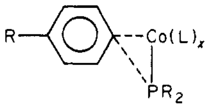

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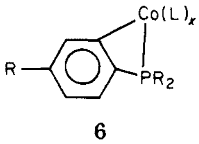

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These findings appear to be relevant to other homogeneous triarylphosphine-modified catalyst systems. We have recently reported the quantitative formation of benzene during $RuCl_2(PPh_3)_3$-catalyzed conversion of primary to secondary amines,[14] and Crabtree has detected 0.8 mol of fluorobenzene per mol of Ir during his studies on cyclohexane dehydrogenation catalyzed by $[IrH_2S_2L_2]SbF_6$ (S = Me_2CO, L = PPh_3) at 150 °C.[15] Our results using phosphinated polystyrene as an "immobilization" medium for $Co_2(CO)_8$ raise questions about previous reports of the recycling of such hydroformylation catalysts.[16]

In conclusion we wish to note that the detection of triarylphosphine decomposition and/or loss of functionality on heterogenized support materials is a much more common reaction than had been previously thought. It is clear that this decompostion pathway is possible for any reaction involving transition-metal–triarylphosphine catalysis.[18]

Acknowledgment. We thank The Dow Chemical Co. for its support of the work at The Pennsylvania State University. We also thank Professors Crabtree and Tanaka for communication of their results prior to publication.

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(8) (a) Fellmann, J. D.; Garrou, P. E.; Withers, H. P.; Seyferth, D.; Trafficante, D. D. *Organometallics* **1983**, *28* 818. (b) Dubois, R. A.; Garrou, P. E.; Hartwell, G. E.; Hunter, D. H. *Ibid.* **1984**, *3*, 95.

(9) For R = Ph in the presence of 1-hexene substrate, 0.93 mol of benzene is produced per mol of cobalt after 8 days. For R = CH_2Ph, in the absence of substrate, 0.89 mol of toluene is produced per mol of cobalt after only 36 h of reaction. Blank reactions show less than 3% of the benzene could be formed via simple thermal degredation at the reaction temperature.

(10) When 1-hexene is present we believe the R_2PH reacts with it to produce R_2P(hexyl) which we also observe in minor amounts by ^{31}P NMR. The reverse observation, i.e., phosphido cobalt clusters reacting under CO/H_2 with 1-hexene to give R_2P(hexyl), has been recently reported.[11]

(11) Harley, A. D.; Guskey, G. J.; Geoffroy, G. L. *Organometallics* **1983**, 2, 53.

(12) At this point we cannot rule out a radical mechanism. We cannot find radical initiators or scavengers that are stable under our reaction conditions. We are continuing our attempts to examine this possibility.

(13) Although a yield of this alcohol has not yet been determined, we did obtain an 11.5% yield of benzyl alcohol from a similar reaction with $Co_2(CO)_8/8PPh_3$.

(14) Jung, C. W.; Fellmann, J. D.; Garrou, P. E. *Organometallics* **1983**, *2*, 1042.

(15) Crabtree, R. H., private communication.

(16) For example, close examination of an earlier report[17] in which recycling was carried out contained analytical data that revealed substantial losses of both Co and P after only a few recycles.

(17) Evans, G. O.; Pittman, C. U.; McMillan, R.; Beach, R. T.; Jones, R. J. *J. Organomet. Chem.* **1974**, *67*, 295.

(18) After this publication was submitted we were informed[19] of similar studies which conclude that decomposition during hydroformylation is in the order $Rh_4(CO)_{12}/PPh_3 > Ru_3(CO)_{12}/PPh_3 > Ru_4(CO)_{12}/PBu_3 \sim Co_2(CO)_8/PPh_3 > Ru_3(CO)_{12}/PBu_3 > Co_2(CO)_8/PBu_3$.

(19) Tanaka, M., private communication.

Transfer of Ethylidene from η^5-$C_5H_5(CO)_2Fe{=}CHCH_3^+$ to Para-Substituted Styrenes. Loss of Stereochemistry about the C_α–C_β Double Bond of *cis*-β-Deuterio-*p*-methoxystyrene

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Received December 2, 1983

Summary: Transfer of ethylidene from η^5-$C_5H_5(CO)_2Fe{=}CHCH_3^+$ to a series of para-substituted styrenes gives

0276-7333/84/2303-0650$01.50/0