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Preliminary communication

REACTIONS OF $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_5H_5)$ WITH PHOSPHORUS DONOR LIGANDS

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Summary

The course of the reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_5H_5)$ with phosphorus donor ligands depends strongly on the nature of the ligand; products derived from an Arbuzov-like rearrangement or from reduction have been found as well as the expected simple substitution product. The dynamic PMR behavior of $(\eta^5\text{-}C_5H_5)Fe(CO)(P(OPh)_3)(\eta^1\text{-}C_5H_5)$ has been examined.

In connection with a study on deprotonation of η^1-cyclopentadienyl-transition metal complexes (1), we wished to examine substituted complexes $(\eta^5\text{-}Cp)Fe(CO)L(\eta^1\text{-}Cp)$ (Cp = C_5H_5). While the parent compound $(\eta^5\text{-}Cp)Fe(CO)_2(\eta^1\text{-}Cp)$ (I) was first prepared over twenty years ago (2) and has been extensively studied with regard to its temperature-dependent NMR behavior (3), no substituted derivatives or any extensive chemistry of I have been reported. We find that attempts to prepare such derivatives by the direct reaction of phosphine or phosphite ligands with I[*] give unexpected products depending upon the nature of the

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[*] An alternate route, treatment of $(\eta^5\text{-}Cp)Fe(CO)LI$ with NaCp, gave no reaction at all (THF; 25°; 24 hours; L = PPh_3 or $P(OMe)_3$). This is somewhat surprising, since $(\eta^5\text{-}Cp)Fe(CO)_2I$ reacts with NaCp in minutes at <0°, and $(\eta^5\text{-}Cp)Fe(CO)(PPh_3)I$ reacts readily with lithium alkyls (7).

ligand used, and here present a preliminary account of these results.

Substitution reactions of the alkyl complexes (η^5-Cp)Fe(CO)$_2$R usually require elevated temperatures or irradiation for reasonable rates, and generally proceed smoothly (complicated only by carbonyl insertion in some cases) under these conditions (4-6). In contrast, similar reactions of I proceed even at room temperature and give at least three quite different pathways, as illustrated by the following:

a) Treatment of a concentrated benzene solution of I with excess P(OMe)$_3$ results in rapid gas evolution and a color change from red-orange to yellow. Reaction is complete within 10 minutes, giving (η^5-Cp)Fe(CO)(P(OMe)$_3$)(P(O)(OMe)$_2$) (II) and methylcyclopentadiene, both in virtually quantitative yield (by NMR). Complex II, which was previously obtained as an inseparable mixture with (η^5-Cp)Fe(CO)$_2$(P(O)(OMe)$_2$) from the reaction of P(OMe)$_3$ with (η^5-Cp)Fe(CO)$_2$Cl (8), was isolated as a yellow-white oil after evaporation of volatiles by precipitation from toluene-hexane. Its NMR, which was not reported, consists of the following signals (benzene solution): 5.43 τ, triplet (J_{PH} = 1.0 Hz), η^5-C_5H_5; 6.30 τ, two doublets (J_{PH} = 11.0 Hz), PO(OCH$_3$)$_2$; 6.44 τ, doublet (J_{PH} = 11.5 Hz), P(OCH$_3$)$_3$. Two doublets (separation .015 ppm) are observed for the phosphonate ligand since the chiral center at iron makes the two methyl groups non-equivalent.

b) A similar reaction of I with PMePh$_2$ in acetone results in a rapid deepening of color to dark red; the only identifiable product formed is the phosphine-free dimer [(η^5-Cp)Fe(CO)$_2$]$_2$. Also formed is a light-colored insoluble material, and the NMR exhibits several very broad peaks in addition to the sharp signal due to the dimer. The solid is soluble in dilute acid but not in any organic solvents and appears to be an Fe(II) salt. In other solvents (benzene, chloroform) this reaction is much slower.

c) Reaction of I with $P(OPh)_3$ proceeds slowly in benzene to give, as major product, the desired substitution product $(\eta^5\text{-Cp})Fe(CO)(P(OPh)_3)(\eta^1\text{-Cp})$ (III); at least one other product, exhibiting broad signals similar to those observed in b), is also formed. III was separated from this side product and unreacted starting materials by repeated chromatography on alumina, and obtained as an orange crystalline solid from hexane. (Analysis: Calculated for $C_{29}H_{25}FeO_4P$: C, 66.43; H, 4.81; Found: C, 66.35; H, 5.01). It has predictable IR (ν_{CO} = 1935 cm^{-1}, Nujol) and NMR spectral properties. The dynamic NMR behavior of III is quite similar to that reported for I: at ambient temperatures (acetone-d_6 solution) two doublets are observed, at 6.51 τ (J_{PH} = 0.8 Hz, η^5-Cp) and 4.24 τ (J_{PH} = 1.8 Hz, η^1-Cp). On cooling, the latter signal broadens, collapses, and grows up (below -50°) as two equal intensity broad signals at 3.46 τ and 3.84 τ. The low field signal is always the broader of the two, as is the case for I (3). No signal was observed for the proton on carbon bonded to Fe; from the relative shifts it appears that this is probably obscured by the η^5-Cp signal. Broadening of all peaks became serious before a limiting low-temperature spectrum could be reached; because of this and other complications* reliable kinetic parameters could not be calculated, but an estimate of the activation energy (using line widths in the fast-exchange region and neglecting the above-mentioned complicating factors) gives a value of 11 kcal/mole, in reasonable agreement with values determined for I (3).

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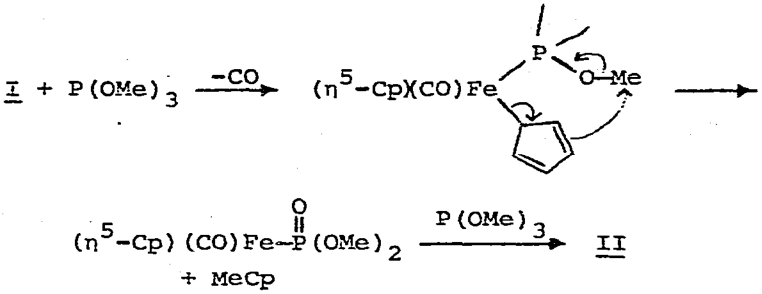
*One of the factors in the line width is the P-H coupling, which will almost certainly be different for the various protons in the η^1-Cp; also conformational isomerism about the Fe-C bond is likely to affect this coupling (9). In fact, slowing of this rotation may be responsible for the general broadening observed at low temperatures; similar broadening has been found for other $(\eta^5\text{-Cp})Fe(CO)(PR_3)$(alkyl) complexes (10,11). Finally, because of the chiral iron center, all five protons on the η^1-Cp should in principle be non-equivalent at low temperature (12).

Formation of II (among other products) from the reaction of $P(OMe)_3$ with $(\eta^5\text{-Cp})Fe(CO)_2Cl$ had been suggested to proceed *via* displacement of Cl^- by $P(OMe)_3$, followed by attack of Cl^- at a methyl group on the cationic complex to give the phosphonate group plus methyl chloride in an Arbuzov-like reaction (8). The analogous process in the present case would involve displacement of Cp^- which does not appear attractive; also it should be noted that II is the only product formed from I, even when an insufficient amount of $P(OMe)_3$ is used, whereas with the chloride II is a minor product, the major one being $(\eta^5\text{-Cp})Fe(CO)_2(P(O)(OMe)_2)$ (8). This suggests that the first step in the reaction of I with $P(OMe)_3$ is CO displacement according to the following scheme:



wherein all steps subsequent to CO displacement must be relatively fast. For $P(OPh)_3$ the Arbuzov-like process would involve an unfavorable nucleophilic attack on a phenyl group, so the substitution product III is stable and can be isolated. The reasons for the apparent instability of the $PMePh_2$ substitution product and the mechanism of the observed reduction to $[(\eta^5\text{-Cp})Fe(CO)_2]_2$ are unclear.

The facility of these reactions, even at room temperature, seems to imply that loss of CO is a much more favorable process

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[*] Rapid CO-replacement reactions have also been reported for $(\eta^5\text{-Cp})Fe(CO)_2H$; this reacts with phosphorus ligands even at -20° (13). A similar enhanced reactivity of a hydride complex has been observed for $HRe(CO)_5$; this was shown to be due to a free-radical chain mechanism (14).

for I than for other alkyls (η^5-Cp)Fe(CO)$_2$R;* this is also suggested by the slow decomposition of I to yield ferrocene. This cannot be attributed to any substantial difference in Fe-CO bond strengths, since the CO stretching frequencies for such complexes are all virtually equal (2). It is tempting to propose that CO displacement can be facilitated by interaction of a free double bond of the η^1-Cp with the iron, stabilizing the otherwise coordinatively unsaturated intermediate. Further mechanistic studies on these systems are now in progress.

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References

1. J. A. Labinger, to be submitted for publication.
2. T. S. Piper and G. Wilkinson, J. Inorg. Nucl. Chem., 3 (1956) 104.
3. F. A. Cotton, in "Dynamic Nuclear Magnetic Resonance Spectroscopy" (L. M. Jackman and F. A. Cotton, Eds.), Academic Press, New York (1975) 378-385, and references therein.
4. P. M. Treichel, R. L. Shubkin, K. W. Barnett and D. Reichard, Inorg. Chem., 5 (1966) 1177.
5. A. N. Nesmeyanov, L. G. Makarova and I. V. Polovyanyuk, J. Organometal. Chem., 22 (1970) 707.
6. S. R. Su and A. Wojcicki, J. Organometal. Chem., 27 (1971) 231.
7. D. L. Reger and E. C. Culbertson, Synth. React. Inorg. Metal-Org. Chem., 6 (1976) 1.

8. R. J. Haines, A. L. Du Preez and I. L. Marais, J. Organometal. Chem., 28 (1971) 405.

9. K. Stanley and M. C. Baird, Inorg. Nucl. Chem. Letters, 10 (1974) 1111.

10. J. Thomson, W. Keeney, M. C. Baird and W. F. Reynolds, J. Organometal. Chem., 40 (1972) 205.

11. K. Stanley, R. A. Zelonka, J. Thomson, P. Fiess and M. C. Baird, Can. J. Chem., 52 (1974) 1781.

12. W. G. Kita, M. K. Lloyd and J. A. McCleverty, Chem. Commun., (1971) 420.

13. P. Kalack and P. Poilblanc, C. R. Acad. Sci., Ser. C, 274 (1972) 66.

14. B. H. Byers and T. L. Brown, J. Am. Chem. Soc., 97 (1975) 947.