Journal of Organometallic Chemistry, 286 (1985) C5–C7
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

REPLACEMENT OF CO BY R_3P IN THE CYCLOHEXA-1,3-DIENETRICARBONYLIRON SERIES

A.J. BIRCH and L.F. KELLY

Department of Chemistry, Australian National University, GPO Box 4, Canberra, ACT, 2601 (Australia)

(Received January 2nd, 1985)

Summary

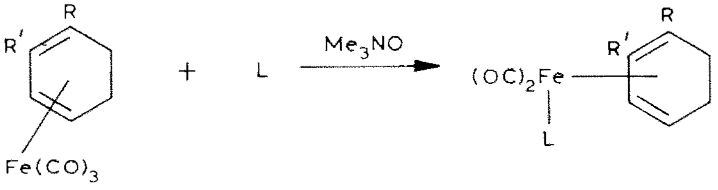
Reaction of tricarbonylcyclohexa-1,3-dieneiron complexes with trimethylamine-*N*-oxide in the presence of trivalent phosphorus donor ligands gives the corresponding $(R_3P)(OC)_2Fe$(cyclohexa-1,3-diene).

Replacement of CO by R_3P in the title series has a number of consequences in terms of the reactivity of the organic group. The decreased electron demand increases the nucleophilic character of the diene e.g. Friedel—Crafts reaction [1], and decreases the electrophilic character of the derived dienyl cation salts [2]. A further feature induced by substituting CO by PR_3 is the potential for asymmetric induction using optically active phosphine ligands. This has been demonstrated in one case using (neomenthyl)$Ph_2PFe(C_6H_8)(CO)_2(1+)$ with cyanide ion [3].

To benefit from the added flexibility using complexes with phosphorus(III) ligands in place of CO requires a general method for their synthesis. Previous methods include direct thermal or photochemical substitution [4] or transfer using $R_3PFe(CO)_4$ [3] or $(R_3P)(CO)_2Fe$(benzylideneacetone) [5]. The former method appears suitable for the unsubstituted cyclohexa-1,3-dienetricarbonyliron complex but for $(2\text{-OMeC}_6H_7)Fe(CO)_3$ the yield was 15% [6]. The second procedure requires the correct conjugated diene, which is often not very accessible

Trimethylamine-*N*-oxide is known [7] to react with a variety of carbonylmetals to produce a coordinatively unsaturated metal species which once formed is then stabilised by Me_3N. In the presence of phosphorus donor ligands the isolated complexes are those due to replacement of CO by the phosphine, presumably through such intermediates.

We have employed Me_3NO as a decarbonylation reagent to prepare a series of substituted (cyclohexa-1,3-diene)$(CO)_2(PR_3)$ complexes. Advantages include the experimental convenience of the reaction, short reaction times and good yields. An excess of amine oxide and phosphine is required which results in formation of the phosphine oxide as an easily removed side product*. Table 1 shows the reactions performed. Of interest is the apparent difference in rates of replacement due to the presence of the various functional groups. The trend observed here is similar to that previously noted in connection with rates of nucleophilic attack on corresponding substituted (dienyl)$Fe(CO)_3$ cations [8]. Seemingly then, electronic effects of ring substituents influence the reactivity of the complexing group just as variation in the complexing group affects that of the organic portion.



(1a–1e) **(2a–2e)**

(a : R = R' = H;
b : R = H, R' = OMe;
c : R = OMe, R' = H;
d : R = H, R' = CO_2Me;
e : R = CO_2Me, R' = H)

TABLE 1

Materials		Time (h)	Yield (%)	Product
(1)	L			
1a	Ph_3P	2	64	2a, $L = PPh_3$
1b	Ph_3P	6	48	2b, $L = PPh_3$
1c	Ph_3P	6	54	2c, $L = PPh_3$
1d	Ph_3P	1	78	2d, $L = PPh_3$
1e	Ph_3P	1	81	2e, $L = PPh_3$
1a	(Neomenthyl)PPh_2	2	68	2a, $L = (C_{10}H_{19})PPh_2$

---

*A typical procedure is as follows: Trimethylamine-*N*-oxide (0.5 g) was added to a stirred solution of the complex 1a, (0.55 g) and neomenthyldiphenylphosphine (0.9 g) in acetone (20 ml). The mixture was vigorously stirred and heated at reflux during 2 h. After this time TLC (SiO_2, 10% EtOAc/hexane) showed a newly formed spot, as well as some remaining phosphine and complex. A further portion of Me_3NO (0.2 g) was added and reflux continued for 1 h after which TLC indicated the reaction to be substantially complete. Ether (20 ml) was added to the cooled mixture which was then filtered and evaporated to leave a yellow solid. A mixture (25 ml) of hexane and ethyl acetate (10%) was added and the resulting white solid was removed by filtration. Evaporation of the yellow solution gave a yellow oily solid which was chromatographed on silica gel using 10% ethyl acetate in hexane as eluent. Isolation of the yellow band gave the product 2a ($L = C_{10}H_{19}PPh_2$; 0.9 g, 70%) as an oil. Spectral properties were identical with those already recorded [3].

Acknowledgements. We thank the Australian Research Grants Scheme for support.

References

1 A.J. Birch, W.D. Raverty, S.Y. Hsu, and A.J. Pearson, J. Organomet. Chem., 260 (1984) C59.
2 L.A.P. Kane-Maguire, J. Chem. Soc., A, (1971) 1602.
3 J.A.S. Howell and M.J. Thomas, J. Chem. Soc. Dalton Trans., (1983) 1401.
4 P.L. Pauson, J. Organomet. Chem., 5 (1966) 73; B.F.G. Johnson, J. Lewis and M.V. Twigg, J. Chem. Soc. Dalton Trans., (1974) 2546.
5 For leading references see J.A.S. Howell, J.C. Kola, D.T. Dixon, P.M. Burkinshaw, and M.J. Thomas, J. Organomet. Chem., 266 (1984) 83.
6 A.J. Pearson and P.R. Raithby, J. Chem. Soc. Dalton Trans., (1981) 884.
7 F. Birencwaig, H. Shamai, and Y. Shvo, Tetrahedron Letts., (1979) 2947 and ref. therein.
8 A.J. Birch, D. Bogsanyi and L.F. Kelly, J. Organomet. Chem., 214 (1981) C39.