

Alkylation and Acylation of Co-ordinated Tertiary Phosphines: the Nucleophilic Substitution of the Carbanions derived from $[M(CO)_4(Ph_2PCH_2PPh_2)]$ ($M = Cr, Mo, or W$)

Subhi Al-Jibori and Bernard L. Shaw*

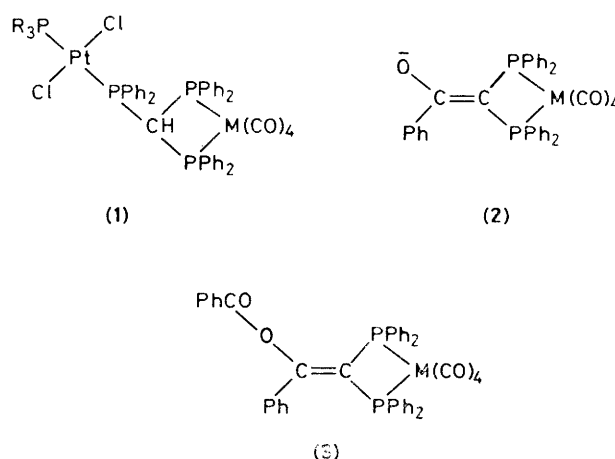
School of Chemistry, The University, Leeds LS2 9JT, U.K.

Complexes of the type $[M(CO)_4(Ph_2PCH_2PPh_2)]$ are readily deprotonated by strong bases and the resultant carbanions attacked by nucleophiles such as MeI, EtI, $CH_2 : CHCH_2Cl$, $PhCH_2Cl$, Me_3SiCl , Ph_2PCl , $PhCOCl$, or MeC_6H_4COCl , to effect C-substitution.

There is much interest in bis(diphenylphosphino)methane (dppm) as a ligand in co-ordination chemistry. It can be monodentate or bidentate towards one metal atom and can also give many complexes containing metal-metal bonds: these metal-metal bonds are broken by small molecules, or atoms, to give complexes with 'A-frame' structures.¹ The corresponding ion, $[Ph_2PCHPPh_2]^-$ is also an excellent ligand for transition metals: in addition to forming a series of very stable mononuclear complexes it can also bridge two or three metal atoms.²⁻⁶ The crystal structures of two mononuclear platinum(II) complexes of this ionic ligand show that the PtP_2C moiety forms a planar 4-membered ring, *i.e.* Pt and C are not directly bonded,^{6,7} although one would expect the negative charge to be extensively delocalised. We investigated the carbanion reactivity of this ligand, when chelated to a transition metal, and chose to study derivatives of Group 6 metal carbonyls.

The complexes $[M(CO)_4(dppm)]$ ($M = Cr, Mo, or W$) were prepared by thermal methods⁸ or by using phase-transfer catalysis.⁹ When treated with one mol. equiv. of a strong base such as Bu^tLi in the presence of $Me_2NCH_2CH_2NMe_2$ (TMED) in diethyl ether-benzene, a yellow suspension was obtained which, when treated with MeI, EtI, $CH_2 : CHCH_2Cl$, or $PhCH_2Cl$, readily gave the corresponding C-mono-alkylated derivatives $[M(CO)_4(Ph_2PCHRPPH_2)]$ in 70–85% yield. Moreover treatment of $[Cr(CO)_4(dppm)]$ with 4 equiv. of MeLi-TMED for 1 h at 20 °C, followed by 4 equiv. of MeI at 70 °C, gave the dimethylated complex $[Cr(CO)_4(Ph_2PCMe_2PPh_2)]$ in 89% yield. These are the first examples of the alkylation of co-ordinated phosphines and must involve carbanion intermediates. Clearly dppm is a favourable case but strong, non-nucleophilic (*i.e.* bulky) bases should deprotonate less activated phosphine ligands which could then be alkylated: more powerful alkylating agents than MeI might be necessary. We have shown that *mer*- $[IrCl_3(PMe_2Ph)_3]$ is deprotonated by $LiNPr_3$ *etc.* but the resultant carbanion attacks the iridium, with displacement of the chloride ion, to

give $[IrCl_2\{PMePh(CH_2)\}(PMe_2Ph)_2]$, containing a 3-membered ring.¹⁰ Recently it has been reported that *trans*- $[Ni\{C_6H_3(OMe)_2\}_2(PMe_3)_2]$ is deprotonated by Bu^tLi and,



on treatment with D_2O , two of the PMe hydrogen atoms are replaced by deuterium.¹¹

We have also treated the carbanions, $[M(Ph_2PCHPPH_2)(CO)_4]^-$, with the nucleophiles Me_3SiCl or Ph_2PCl to give the corresponding derivatives. The unco-ordinated phosphorus atom of the η^2 -triphosphine derivatives $[M\{CH(PPh_2)_3\}(CO)_4]$ is readily converted into the corresponding phosphine oxide (with H_2O_2) or phosphine sulphide (with S_8) and it also co-ordinates to other metal ions, *e.g.* when treated with platinum(II) bridge complexes, $[Pt_2Cl_4(PR_3)_2]$, complexes of type (1) form readily.

Thus the carbanions $[M(Ph_2PCHPPH_2)(CO)_4]^-$ are readily attacked by a variety of nucleophiles, specifically at the central (CH) carbon atom. This contrasts with the free anion $[Ph_2PCHPPH_2]^-$, which is ambident and can be attacked at carbon or phosphorus atoms; Ph_2PCl attacks it mainly at carbon whereas the aliphatic analogues, R_2PCl , attack it predominantly at phosphorus,¹² as does benzyl chloride.² Uncomplexed C-substituted derivatives of dppm are therefore often difficult to synthesise although as ligands they might be expected to show interesting steric and conformational effects, not shown by dppm itself. We suggest that syntheses of such C-substituted derivatives using complexed dppm,

might be quite widely applicable provided that suitable deprotonating and alkylating agents are used.

One could probably attach a variety of functional groups to the central carbon atom of dppm using the co-ordinated carbanion. We have synthesized the benzoyl derivatives; and *p*-toluoyl treatment of $[\text{Cr}(\text{dppm})(\text{CO})_4]$ with Bu^nLi in ether, and subsequent treatment with benzoyl chloride gives the *C*-benzoyl derivative $[\text{Cr}\{\text{Ph}_2\text{PCH}(\text{COPh})\text{PPh}_2\}(\text{CO})_4]$ in 92% yield; similarly for Mo and W. TMED should be avoided in this reaction as, when used, a mixture of the benzoyl and the methyl derivatives is obtained; the methyl group can only have come from the TMED, probably *via* an intermediate such as $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2(\text{COPh})\text{Cl}^-$. TMED is very frequently added to Bu^nLi in synthesis to increase the basicity and reactivity but, in view of our result, one cannot assume it is always inert in subsequent reactions of the carbanion. The *C*-benzoyl derivatives $[\text{M}\{\text{Ph}_2\text{PCH}(\text{COPh})\text{PPh}_2\}(\text{CO})_4]$ immediately give the enolate ions (2) when treated with base, *e.g.* sodium ethoxide. Subsequent treatment with benzoyl chloride gives the *O*-benzoyl enolate derivatives (3): no *C,C*-dibenzoyl derivatives could be detected.

We are currently extending studies on nucleophilic attack on co-ordinated tertiary phosphine carbanions to other systems, and developing the chemistry of complexes of functionalised dppm. A very unusual reaction, *viz.* a ring expansion, 4- to 7-membered, of a derivative of $\text{Ph}_2\text{PCH}(\text{COPh})\text{PPh}_2$, is reported in the following communication.

We thank the Government of Iraq and the Science and Engineering Research Council for support.

Received, 16th November 1981; Com. 1332

References

- 1 M. P. Brown, S. J. Cooper, A. A. Frew, L. Manojlovic-Muir, K. W. Muir, R. J. Puddephatt, K. R. Seddon, and M. A. Thompson, *Inorg. Chem.*, 1981, **20**, 1500, and references cited therein.
- 2 K. Issleib and H. P. Abicht, *J. Prakt. Chem.*, 1970, **312**, 456.
- 3 K. Issleib, H. P. Abicht, and H. Winkelmann, *Z. Anorg. Allg. Chem.*, 1972, **388**, 89.
- 4 A. Camus, N. Marsich, G. Nardin, and L. Randaccio, *J. Organomet. Chem.*, 1973, **60**, C39.
- 5 G. M. Dawkins, M. Green, J. C. Jeffery, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1980, 1120.
- 6 J. M. Bassett, J. R. Mandl, and H. Schmidbaur, *Chem. Ber.*, 1980, **113**, 1145.
- 7 J. Browning, G. W. Bushnell, and K. R. Dixon, *J. Organomet. Chem.*, 1980, **198**, C11.
- 8 S. O. Grim, W. L. Briggs, R. C. Barth, C. A. Tolman, and J. P. Jesson, *Inorg. Chem.*, 1974, **13**, 1095.
- 9 K. Y. Hui and B. L. Shaw, *J. Organomet. Chem.*, 1977, **124**, 262.
- 10 S. Al-Jibori, C. Crocker, W. S. McDonald, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1981, 1572.
- 11 M. Wada, *J. Chem. Soc., Chem. Commun.*, 1981, 680.
- 12 R. Appel, M. Wander, and F. Knoll, *Chem. Ber.*, 1979, **112**, 1093.