Polyhedron Vol. 11, No. 1, pp. 135–137, 1992
Printed in Great Britain

0277–5387/92 \$5.00+.00
© 1992 Pergamon Press plc

COMMUNICATION

A NEW CLASS OF CHELATING DIPHOSPHITE: SYNTHESIS AND COMPLEXATION OF THE SILYLATED DIPHOSPHITES $[(R^1O)_2PO]_2SiR^2R^3$ (R^1 = Me, Et; R^2, R^3 = Me, Ph, H, —CH=CH$_2$)

TERENCE P. KEE* and MUKESH T. PATEL

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

(*Received* 2 *September* 1991; *accepted* 2 *October* 1991)

Abstract—A general synthesis for a novel class of chelating diphosphites $[(R^1O)_2PO]_2SiR^2R^3$ ($R^2 = R^3$ = Me; $R^2 = R^3$ = Ph; R^2 = Me, R^3 = Ph; R^2 = Me, R^3 = H; R^2 = Me, R^3 = —CH=CH$_2$; R^1 = Me, Et) is reported. These diphosphite compounds react with $MnBr(CO)_5$ giving the complexes *fac*-$MnBr(CO)_3\{[R^1O)_2PO]_2SiR^2R^3\}$.

Chelating tertiary phosphine ligands are used extensively in coordination and organometallic chemistry where their ability to affect the stereoelectronic environment around a metal atom has been exploited in both stoichiometric and catalytic transition metal mediated processes.[1] However, despite the applications of tertiary phosphites as highly active co-catalysts in alkene hydroformylation[2] and dimerization[3] reactions, chelating tertiary phosphites have received much less attention.[4] We are currently investigating the chemistry of silylated organophosphorus compounds[5] and wish to report here a class of novel silyl diphosphite compounds capable of chelating to transition metals.

EXPERIMENTAL

All manipulations of air- and/or moisture-sensitive compounds were performed under dry nitrogen using Schlenk and cannula techniques. Solvents were dried by standard methods, distilled and degassed prior to use. IR spectra were recorded between KBr windows using a Perkin–Elmer 257 grating spectrophotometer. NMR spectra were obtained on JEOL FX90Q, JEOL FX100 and Bruker AM 400 instruments. Both $(R^1O)_2P(=O)H$ and $Cl_2SiR^2R^3$ reagents were distilled before use and NEt_3 was purified by passage down a short column of basic alumina (Brockmann Grade I).

Synthesis of $[(MeO)_2PO]_2SiMe_2$ (**1a**)

Cl_2SiMe_2 (0.35 g, 2.72 mmol) was added dropwise at room temperature to a stirred mixture of $(MeO)_2P(=O)H$ (0.6 g, 5.45 mmol) and NEt_3 (1.45 g, 14.3 mmol) in toluene solvent (30 cm^3). The initially clear solution became cloudy within several seconds of adding the silicon reagent as $NHEt_3Cl$ precipitated. After stirring at room temperature for 48 h, the mixture was filtered, the residue washed with light petroleum ether (2 × 10 cm^3) and all volatiles removed under reduced pressure to afford the product as a clear, mobile liquid. Yield 0.73 g, 96%. ^1H NMR (C_6D_6): δ 3.29 [m, 12H, $J(P$—H) 11 Hz, CH_3O], 0.22 [s, 6H, $Si(CH_3)_2$]. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 47.7 [m, J(P—C) 9 Hz, CH_3O], 0.6 [s, $Si(CH_3)_2$]. Diphosphites **1b–j** were prepared using analogous procedures, being isolated in yields between 78–99%. All were found to be of sufficient purity for synthetic purposes.

Synthesis of fac-$MnBr(CO)_3\{[(MeO)_2PO]_2SiMe_2\}$ (**2a**)

A 0.32 M solution (2.28 cm^3, 0.73 mmol) of **1a** in toluene was added to a suspension of $MnBr(CO)_5$ (0.2 g, 0.73 mmol) in toluene (10 cm^3) at room temperature. Within 5 min the remaining yellow solid had dissolved to an orange solution. After stirring overnight the mixture was filtered, concentrated under reduced pressure and cooled to −35°C to afford the product **2a** as yellow crystals

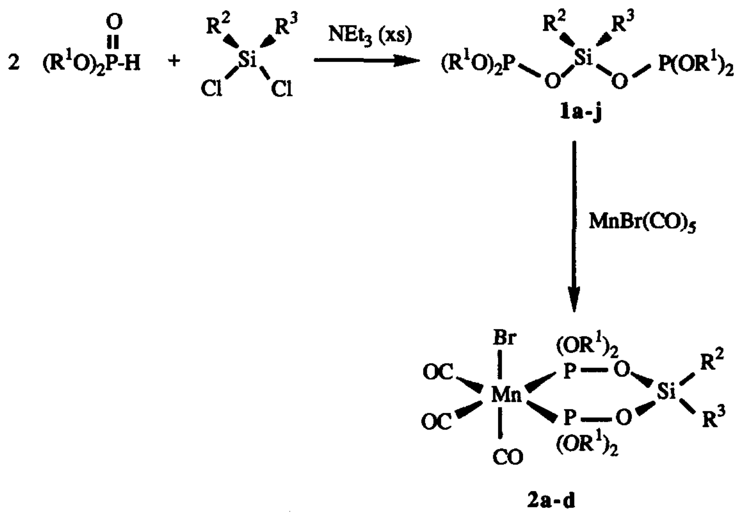
---

* Author to whom correspondence should be addressed.

which were isolated, washed with light petroleum ether and dried *in vacuo*. Yield, 0.21 g, 59%. Found: C, 21.8; H, 3.7. Calc. for $C_9H_{18}O_9SiP_2MnBr$: C, 21.8; H, 3.7%. ^{1}H NMR (C_6D_6): δ 3.67 [m, 6H, J(P—H) 11 Hz, $C\mathit{H}_3O$], 3.24 [m, 6H, J(P—H) 11 Hz, $C\mathit{H}_3O$], 0.46 [s, 3H, $SiC\mathit{H}_3$], 0.02 [s, 3H, $Si(C\mathit{H}_3)$]. Complexes **2b–d** were prepared and characterized analogously.

RESULTS AND DISCUSSION

Diphosphites **1a–j** are readily isolated in high yields as clear, mobile liquids by a convenient, single step route using inexpensive starting materials (see Scheme 1 and Experimental for details of a representative example). The flexibility of this synthesis allows for control over the substituents on both phosphorus and silicon atoms: in particular, compounds **1d** and **1e** contain the potentially useful Si—CH=CH$_2$ and Si—H functionalities whose chemistry we are exploring currently. The $^{31}P\{^1H\}$ NMR spectra of **1a–j** consist of single resonances in the region expected for tertiary phosphite compounds[6] and show little sensitivity to the nature of the substituents on silicon (Scheme 1). Complexation of these diphosphites to transition metals occurs readily: partial NMR and IR data for representative examples of complexes of the form *fac*-



Scheme 1.

Compound	R^1	R^2	R^3	$^{31}P\{^1H\}$[a]	IR (cm^{-1})[b]
1a	Me	Me	Me	126.6	940(s, br)[c]
1b	Me	Ph	Ph	126.2	950(s, br)[c]
1c	Me	Me	Ph	126.3	940(s, br)[c]
1d	Me	Me	CH=CH$_2$	126.2	978(s, br)[c]
1e	Me	H	Me	126.8	2175(m),[d] 950(s, br)[c]
1f	Et	Me	Me	125.3	925(s, br)[c]
1g	Et	Ph	Ph	124.8	930(s, br)[c]
1h	Et	Me	Ph	125.3	928(s, br)[c]
1i	Et	Me	CH=CH$_2$	125.3	980(s, br)[c]
1j	Et	H	Me	125.9	2185(m),[d] 930(s, br)[c]
2a	Me	Me	Me	149.3	2050, 1981, 1941[e]
2b	Me	Ph	Ph	149.9	2048, 1980, 1941[e]
2c	Me	Me	Ph	149.3	2050, 1982, 1943[e]
2d	Me	Me	CH=CH$_2$	149.4	2048, 1980, 1942[e]

[a] All values reported in C_6D_6 solvent at ambient temperature as δ in ppm from 85% H_3PO_4 (0 ppm).

[b] **1a–j** as thin films, **2a–d** in CH_2Cl_2 solution. m = medium, s = strong, br = broad.

[c] ν(POSi).

[d] ν(SiH).

[e] ν(CO), all bands are strong.

$MnBr(CO)_3\{[(MeO)_2PO]_2SiR^2R^3\}$ are given in Scheme 1, which are consistent with a facial geometry: the synthesis of **2a** is given in the Experimental. Related silylated diphosphite complexes of molybdenum have been reported recently, but the free diphosphites were not prepared.[7]

The extension of this convenient synthetic route to the preparation of other polyphosphites and studies of their coordination, catalytic and synthetic chemistry will form the basis of future reports.

REFERENCES

1. L. H. Pignolet (Editor), *Homogeneous Catalysis with Metal–Phosphine Complexes*. Plenum Press, New York (1983).
2. P. W. N. M. Van Leeuwen and C. F. Roobeek, *J. Organomet. Chem.* 1983, **258**, 343.
3. P. W. N. M. Van Leeuwen and C. F. Roobeek, *Tetrahedron* 1981, **37**, 1973.
4. (a) J. R. Bleeke, A. J. Donaldson and W.-J. Peng, *Organometallics* 1988, **7**, 33; (b) M. J. Baker, K. N. Harrison, A. G. Orpen, P. G. Pringle and G. Shaw, *J. Chem. Soc., Chem. Commun.* 1991, 803; (c) F. A. Cotton, R. J. Haines, B. E. Hanson and J. C. Sekutowski, *Inorg. Chem.* 1978, **17**, 2010.
5. K. M. Cooke, T. P. Kee, A. L. Langton and M. Thornton-Pett, *J. Organomet. Chem.*, in press.
6. D. G. Gorenstein (Editor), *Phosphorus-31 NMR: Principles and Applications*, Ch. 18. Academic Press, New York (1984).
7. G. M. Gray, F. P. Fish, D. K. Srivastava, A. Varshney, M. J. van der Woerd and S. E. Ealick, *J. Organomet. Chem.* 1990, **385**, 49.