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The Reaction of Trimethyltin Hydroxide with Metal–Coordinated PCl_3: Formation of a Tris(trimethylstannyl)phosphite Complex

W.-W. DU MONT and M. GRENZ

Institut für Anorganische und Analytische Chemie der Universität Berlin, D 1000 Berlin 12, F.R.G.

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In previous papers [1] we reported the synthesis of functionally substituted tin complexes by substitution reactions at stannous chloride complexes of pentacarbonyl chromium, molybdenum and tungsten. Recently, trimethyltin hydroxide gave the desired Cl/OH exchange providing a suitable way of preparation for metal complexes of stannous hydroxide [2]. The corresponding reaction of $W(CO)_5GeCl_2$–THF with trimethyltin hydroxide gave not only Cl/OH exchange but also an esterification leading to (W)–Ge–O–$SnMe_3$ moieties [3]. From this we were interested whether the corresponding reaction of Me_3SnOH with transition metal complexes of PCl_3 would be a new access to L_nM–$P(OH)_3$ complexes [4], or M–P–O–$SnMe_3$ moieties would be formed. In the case of a pentacarbonyl tungsten complex ^{31}P NMR shifts and couplings like $^1J(PW)$ and $^2J(SnP)$ should allow a clear distinction between different cases of $(CO)_5W$–$P(OH)_n(OSnMe_3)_{3-n}$.

The pentacarbonyl tungsten phosphorustrichloride complex was mixed with three equivalents of trimethyltin hydroxide and stirred overnight in toluene. After removal of the solvent under reduced pressure the residue was heated to 50 °C at 1 mbar (attempted sublimation of Me_3SnCl). This led to a crude product of $W(CO)_5P(OSnMe_3)_3$ (*I*) that still contained about 10% of another complex with the structural moiety $W(CO)_5P(OSnMe_3)_2O$– (δ ^{31}P 109 ppm, $^1J(^{183}W^{31}P)$ 360 Hz, $^2J(^{119}Sn^{31}P)$ 110 Hz, integrals of the $^{117,119}Sn$ satellites consistent with a $P(OSn)_2$ case).

I was further purified by sublimation at 90 °C/0.1 mbar to give slightly yellowish crystals that gave correct analytical data for $W(CO)_5P(OSnMe_3)_3$. The structure of the new tris(trimethylstannyl)phosphite complex was unambiguously confirmed by ^{31}P NMR spectroscopy. The spectrum (Table I) consists of a main singlet at 98 ppm with tungsten satellites (doublet $^1J(^{183}W^{31}P)$ 350.3 Hz, rather small for a phosphite complex) and pairs of tin satellites (doublets $^2J(^{117};^{119}Sn^{31}P)$ with the correct integral fitting to a $P(OSn)_3$ structure).

In a high resolution ^{31}P NMR spectrum we detected also further 'tin satellites' due to the outer branches of ^{31}P NMR triplets arising from $^2J(PSn)$ of molecules containing two NMR-active tin nuclei (two ^{119}Sn: $^2J(PSn)$ 103.9 Hz, two ^{117}Sn: $^2J(PSn)$ 99.3 Hz, one ^{119}Sn and one ^{117}Sn: double relative intensity, satellite peaks 101.6 Hz from the ^{31}P main signal).

The carbonyl stretching vibration pattern of *I* (Table I) is consistent with a rather undistorted local C_{4v} symmetry of $W(CO)_5$–P. *I* did not give a sharp melting point and a sample heated to the melt (150 °C) showed signals of decomposition products in the Raman spectrum (2015 and 1999 cm^{-1}). The esterification reaction with Me_3SnOH leading to *I* and corresponding germylene complexes as well the hydrolytic behaviour of such compounds are under investigation.

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TABLE I. Properties of $W(CO)_5P(OSnMe_3)_3$ (*I*)*.

Analysis: C found 18.5 (calcd. 18.75); H found 3.0 (calc. 3.03)%

$\nu(CO)$ Infrared: 2050, 1964, 1904 cm^{-1}

Raman: 2057, 1956, 1901 cm^{-1}

^1H NMR $\delta(^1H)$ – 0.2 ppm, $^2J(^1H^{119}Sn)$ 59.2 Hz

^{31}P NMR $\delta(^{31}P)$ 98 ppm; $^1J(^{183}W^{31}P)$ 350.3 Hz; $^2J(^{119}Sn^{31}P)$ 103.8 Hz

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*IR: Perkin-Elmer 457, CsI/nujol; RAMAN: Cary 82; ^1H-NMR: VARIAN EM 360; ^{31}P-NMR: BRUKER WP 80 (FT). Chemical shifts against TMS (^1H) and 85% H_3PO_4 (^{31}P).

References

1 W.-W. du Mont and B. Neudert, *Chem. Ber.*, *111*, 2267 (1978); W.-W. du Mont, *Z. Anorg. Allg. Chem.*, *450*, 57 (1979).

2 W.-W. du Mont and B. Neudert, *Angew. Chem.*, *92*, 561 (1980); *idem*, *Angew. Chem. Int. Ed. Engl.*, *19*, 553 (1980).

3 W.-W. du Mont and G. Rudolph, unpublished results.

4 H. Nöth, H. Reith and V. Thorn, *Z. Anorg. Allg. Chem.*, *458*, 219 (1979).