

## **M(CO)<sub>5</sub>(R<sub>3</sub>P<sub>Te</sub>) (M = Cr, Mo, W; R = Bu<sup>t</sup>): the First Stable Tellurophosphorane Complexes**

**Norbert Kuhn,<sup>\*a</sup> Hans Schumann,<sup>a</sup> and Gotthelf Wolmershäuser<sup>b</sup>**

<sup>a</sup> *Fachbereich 6 (Chemie) der Universität (GH) Duisburg, Lotharstr. 1, D-4100 Duisburg 1, Federal Republic of Germany*

<sup>b</sup> *Fachbereich Chemie der Universität Kaiserslautern, Erwin-Schroedinger-Straße, D-5750 Kaiserslautern, Federal Republic of Germany*

Stable complexes M(CO)<sub>5</sub>(R<sub>3</sub>P<sub>Te</sub>) (M = Cr, Mo, W; R = Bu<sup>t</sup>) are formed by photolysis of M(CO)<sub>6</sub> in the presence of R<sub>3</sub>P=Te; the X-ray crystal structure of W(CO)<sub>5</sub>(Bu<sup>t</sup><sub>3</sub>P<sub>Te</sub>) is reported.

---

Though phosphane chalcogenides R<sub>3</sub>P=X (X = O, S, Se) have been used as ligands in co-ordination chemistry for a long time,<sup>1,2</sup> no tellurophosphorane complexes are mentioned in the literature. Apparently, some experiments starting from trimethyltellurophosphorane gave phosphane complexes and tellurium only.<sup>3</sup>

We have found that irradiation of the hexacarbonyls (**1**) with tri-*t*-butyltellurophosphorane (**2**) in tetrahydrofuran (THF) gives the tellurophosphorane complexes (**3**) in almost quantitative yield. The dark red crystals are fairly stable in air. No tellurium formation could be detected in toluene solution up to 100 °C.

**Table 1.** N.m.r. data of the complexes  $M(\text{CO})_5(\text{R}_3\text{P}\text{Te})$  (**3**) ( $\text{R} = \text{Bu}^t$ ).<sup>a</sup>

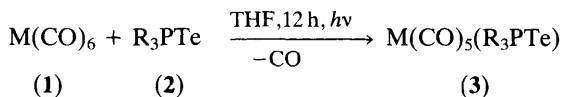
M	<sup>13</sup> C N.m.r. <sup>b,c</sup>			<sup>31</sup> P N.m.r. <sup>d</sup>		<sup>125</sup> Te N.m.r. <sup>e,f</sup>
	$\delta(\text{CO})$	$\delta(\text{qC})$	$\delta(\text{CH}_3)$	$\delta/\text{p.p.m.}$	$J(^{31}\text{P}^{125}\text{Te})$	$\delta/\text{p.p.m.}$
Cr	<i>cis</i> 218.54 (3.4) <i>trans</i> 224.9	41.32 (12.5)	30.78	53.5	1502	-635
Mo	<i>cis</i> 206.8 (3.4) <i>trans</i> 213.09	41.25 (13.7)	30.85	54.7	1602	-749
W	<i>cis</i> 199.44 (3.4) <i>trans</i> 200.4	41.33 (12.8)	30.78	49.9	1600	-770

<sup>a</sup> In  $[\text{C}_6\text{H}_6]$  benzene at 300 K. <sup>b</sup>  $J(\text{PC})$  coupling constants (Hz) in brackets. <sup>c</sup>  $\text{R}_3\text{P}=\text{Te}$ :  $\delta(\text{qC})$  39.63 (14.2),  $\delta(\text{CH}_3)$  31.26. <sup>d</sup>  $\text{R}_3\text{P}=\text{Te}$ :  $\delta$  74.4 p.p.m.,  $J(^{31}\text{P}^{125}\text{Te})$  1600 Hz (from ref. 8). <sup>e</sup> To higher frequency of  $\text{TeMe}_2$ . <sup>f</sup>  $\text{R}_3\text{P}=\text{Te}$ :  $\delta$  -839 p.p.m.

The co-ordination of (**2**) causes a significant low field shift of the CO groups in the <sup>13</sup>C n.m.r. thus indicating the strong donor ability of the tellurophosphorane ligand.<sup>4</sup> In fact, the shift values are comparable to those of the  $M(\text{CO})_5\text{I}^-$  anions.<sup>5</sup>

A medium high field shift can be seen in the <sup>31</sup>P n.m.r. spectra on co-ordination of the ligand (**2**), but the difference between it and that of the unco-ordinated tellurophosphorane seems to be smaller than is observed for the analogous selenophosphorane systems.<sup>6</sup>

In cations of the  $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{R}_3\text{P}=\text{Te})^+$  type we have observed a marked decrease of  $^1J(^{31}\text{P}^{125}\text{Te})$  coupling (*ca.* 300 Hz) on co-ordination of the tellurophosphorane.<sup>6</sup> Surprisingly, in (**3**) the  $^1J(^{31}\text{P}^{125}\text{Te})$  coupling constant is nearly unchanged compared with the unco-ordinated ligand (Table 1). This result may be interpreted as an 'end-on' co-ordination using a non-bonding electron pair of the tellurium atom in the



$\text{R} = \text{Bu}^t$

**a**; M = Cr

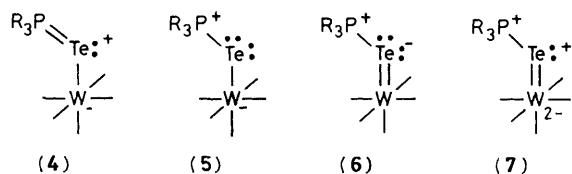
**b**; M = Mo

**c**; M = W

phosphorane ligand. This type of co-ordination has been proved for the thiophosphorane ligand in  $\text{Cr}(\text{CO})_5(\text{Me}_3\text{P}=\text{S})$ .<sup>7</sup>

The <sup>125</sup>Te n.m.r. spectra of (**3**) (Table 1) show a significant downfield shift compared with the unco-ordinated ligand (**2**) which parallels the results obtained from <sup>77</sup>Se n.m.r. measurements of selenophosphorane complexes.<sup>9</sup> The decrease of the co-ordination shift going from the chromium complex (**3a**) to its heavier analogues (**3b**) and (**3c**) is also observed in the  $M(\text{CO})_5\text{TeMe}_2$  series; the co-ordination shift for  $\text{TeMe}_2$  is about 120 p.p.m. greater than for the tellurophosphorane (**2**).<sup>6</sup>

I.r. spectral data of the complexes (**3**) are reported in Table 2. In the CO stretching region five well spaced bands were observed implying that the overall symmetry is not as high as  $C_{4v}$ , the *E* mode no longer being double degenerate. We interpret this divergence from the  $C_{4v}$  selection rules as a

**Table 2.** I.r. spectral data (CO stretching wavenumbers,  $\text{cm}^{-1}$ ) for the complexes  $M(\text{CO})_5(\text{R}_3\text{P}=\text{Te})$  ( $\text{R} = \text{Bu}^t$ ).

M	$A_1''$ (m)	$B_1$ (m)	<i>E</i> (vs)	$A_1'$ (s)
Cr	2052	1986	1937, 1927	1913
Mo	2055	1988	1941, 1937	1912
W	2063	1982	1932, 1927	1909

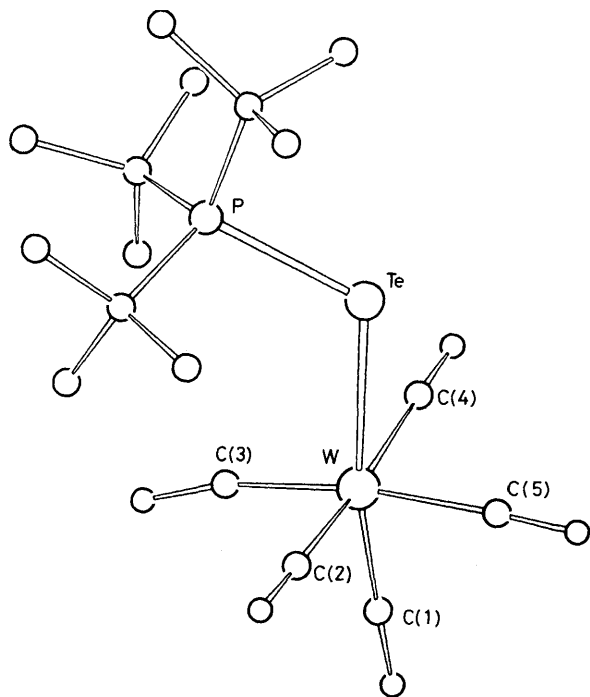
<sup>a</sup> In *n*-hexane at 300 K.

result of the unsymmetrical relation of the tellurophosphorane ligand with the equatorial metal carbonyl groups. In addition, steric interaction cannot be excluded. The lower  $A_1''$  frequencies of (**3**), when compared with some thiophosphorane complexes  $M(\text{CO})_5(\text{R}_3\text{P}=\text{S})$ ,<sup>2</sup> are consistent with the better donor properties of the tellurophosphorane ligand. According to the stronger chalcogen metal bond in (**3**), the tellurophosphorane ligands in the title complexes are not displaced by triphenylphosphane or CO at 80 °C as is reported for the thiophosphorane complexes  $M(\text{CO})_5(\text{R}_3\text{P}=\text{S})$ .<sup>2</sup>

The tellurophosphorane complexes (**3**) may be described in terms of the resonance hybrids (**4**)–(**7**). The *X*-ray structure of (**3c**) was performed to provide some insight into the electronic distribution of the  $\text{W}-\text{Te}-\text{P}$  fragment (Figure 1).<sup>†</sup>

The  $\text{C}(1)-\text{W}$  distance in (**3c**) is the shortest one mentioned for a *trans*-CO tungsten bond in  $\text{W}(\text{CO})_5\text{L}$  complexes, to our knowledge, and is even about 0.03 Å shorter than that reported for a selenadiazole complex,<sup>10</sup> in which the organic nitrogen donor ligand may be considered to be a strong  $\sigma$ -donor ligand without  $\pi$ -interaction. On the other hand, strong  $\pi$ -acceptor ligands like carbenes cause the *trans*-CO tungsten distance to be increased up to 2.00 Å.<sup>11</sup> Thus we conclude that the resonance hybrid (**7**) based on a tellurium tungsten  $\pi$ -donor interaction predominates. This result is in

<sup>†</sup> *Crystal data*  $\text{W}(\text{CO})_5(\text{R}_3\text{P}\text{Te})$  ( $\text{R} = \text{Bu}^t$ ),  $M = 653.83$ , monoclinic, space group  $P2_1/c$ ,  $a = 15.349(2)$ ,  $b = 14.646(3)$ ,  $c = 19.992(2)$  Å,  $\beta = 91.77(1)^\circ$ ,  $Z = 8$ ,  $D_c = 1.934 \text{ g cm}^{-3}$ . Reflections were collected using  $\text{Mo}-K_\alpha$  radiation in the range  $2^\circ < \theta < 22.5^\circ$ . The structure was solved by Patterson methods and refined by blocked-diagonal least-squares to an *R* value of 0.034 for 4867 absorption corrected independent reflections,  $I > 2\sigma(I)$ . The methyl groups were treated as rigid groups with hydrogen atoms on idealized positions (a common thermal parameter was taken for all H atoms and the C–H bond was fixed to 1.08 Å). Both independent molecules show significant differences for their torsion angles  $\text{W}-\text{Te}-\text{P}-\text{Bu}^t$  but not for bond length and angles. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



**Figure 1.** The structure of  $W(CO)_5(R_3PTe)$  (**3c**). Selected bond lengths (Å) and bond angles (°) averaged for both molecules: W-Te 2.875(1); Te-P 2.439(2); W-C(1) 1.92(1); W-C(2-5) averaged 2.04(1); W-Te-P 120.1(1); C(1)-W-Te 169.6(3).

accordance with the unexpectedly high value for the W-Te-P bond angle ( $120.1^\circ$ ) afforded by an  $sp^2$  type tellurium atom.

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support. We are grateful to Dipl.-Ing. W. Riemer [Max-Planck-Institut für

Strahlenchemie, Mülheim), Dr. K. F. Elgert, and Dipl.-Ing. M. Zähres for n.m.r. spectra and to Prof. Dr. P. Sartori for his kind interest in our work.

Received, 9th April 1985; Com. 465

## References

- 1 N. M. Karayannis, C. M. Mikulski, and L. L. Pytlewski, *Inorg. Chim. Acta Rev.*, 1971, **5**, 69; N. Kuhn and M. Winter, *J. Organomet. Chem.*, 1982, **239**, C1; *ibid.*, 1983, **246**, C80; E. Lindner and W. P. Meier, *ibid.*, 1976, **114**, 67; T. S. Lobana and K. B. Sharma, *Indian J. Chem., Sect. A*, 1983, **22**, 710; J. Browning, G. W. Bushnell, K. R. Dixon, and A. Pidcock, *Inorg. Chem.*, 1983, **22**, 2226 and references cited therein.
- 2 E. W. Ainscough, A. M. Brodie, and A. R. Furness, *J. Chem. Soc., Dalton Trans.*, 1973, 2360; P. M. Boorman, S. A. Clow, D. Potts, and H. Wieser, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 941.
- 3 A. M. Brodie, G. A. Rodley, and C. J. Wilkins, *J. Chem. Soc. (A)*, 1969, 2927.
- 4 B. E. Mann and B. F. Taylor, <sup>13</sup>C NMR Data for Organometallic Compounds, Academic Press, London, 1981.
- 5 W. Malisch and R. Janta, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 211; L. J. Todd, J. R. Wilkinson, J. P. Hickey, D. L. Beach, and K. W. Barnett, *J. Organomet. Chem.*, 1978, **149**, C19; S. S. Woodward, R. J. Angelici, and B. D. Dombek, *Inorg. Chem.*, 1978, **17**, 1634.
- 6 N. Kuhn and H. Schumann, unpublished work.
- 7 E. N. Baker and B. R. Reay, *J. Chem. Soc., Dalton Trans.*, 1973, 2205.
- 8 W. W. du Mont and H. J. Kroth, *Z. Naturforsch., Teil B*, 1981, **36**, 332.
- 9 I. J. Colquhoun and W. McFarlane, *J. Chem. Soc., Dalton Trans.*, 1981, 658; S. O. Grim, E. D. Walton, and L. C. Satek, *Aust. J. Chem.*, 1980, **58**, 1476.
- 10 V. Bätzel and R. Boese, *Z. Naturforsch., Teil B*, 1981, **36**, 172.
- 11 C. P. Casey, T. J. Burckhard, C. A. Bunnell, and J. C. Calabrese, *J. Am. Chem. Soc.*, 1977, **99**, 2127; E. O. Fischer, F. J. Gammel, J. O. Besenhard, A. Frank, and D. Neugebauer, *J. Organomet. Chem.*, 1980, **191**, 261.