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Preliminary communication

Synthesis of a tantalum complex containing a side-bonded diphenyldiphosphene

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Abstract

The trihydrides Cp_2MH_3 (M = Nb, Ta) react with PPh_2H. The niobium derivative gives the expected monohydruro complex $Cp_2Nb(H)PPh_2H$, whereas Cp_2TaH_3, gives the side-on diphenyl diphosphene $Cp_2Ta(H)(PPh)_2$.

It is well-known that diorganophosphenes are unstable unless they bear very bulky substituents or are bonded to a transition metal moiety [1]. Several ligation modes are possible, depending on whether the phosphorus lone pairs or the double bond are involved [2]. We report here the unexpected synthesis of a tantalum π-bonded diphenyldiphosphene complex which represents the first example of a diphosphene bonded to an early transition metal.

With the aim of making niobium or tantalum monohydrido complexes **1** by the reaction shown in eq. 1 the trihydride Cp_2MH_3 (M = Nb or Ta) and PPh_2H were allowed to react in boiling toluene.

$$Cp_2MH_3 + PPh_2H \xrightarrow[\Delta]{H_2} Cp_2M(H)PPh_2H \qquad (1)$$

The expected niobium derivative **1** was indeed formed (but in low yield), and it was characterized by its analytical and spectroscopic data: (^1H NMR (C_6D_6): δ 7.7–7m (10H) Ph; 4.44d (10H) Cp, J 2.5 Hz; 6.34d (1H) P–H, J 321 Hz; −7.37d (1H) Nb–H, J 25.5 Hz).

In the case of the reaction of Cp_2TaH_3, however, a brown solid was isolated after work-up: this air-sensitive compound, **2**, is soluble in common organic solvents except hydrocarbons. Its analytical and spectroscopic data differ markedly from those of $Cp_2Nb(H)PPh_2H$: the analysis is consistent with the molecular formula $C_{22}H_{21}P_2Ta$ and the mass spectrum exhibits, inter alia, a molecular ion at *m/e* 528 and a prominent peak at *m/e* 312 assignable to the fragment $[M - P_2Ph_2]^+$. The ^1H NMR spectrum shows three sets of signals: a complex pattern of phenyl hydrogen resonances (10H) at 7.6–6.9; two doublets due to the cyclopentadienyl hydrogens at

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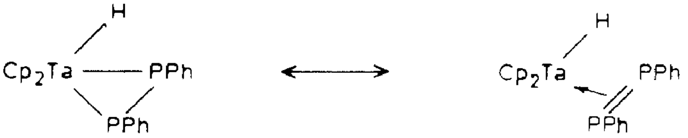
4.5 (5H, J 2.1 Hz) and 4.35 (5H, J 1.5 Hz), and one doublet of doublets at -0.9 ppm (J 42 and 3.5 Hz).

The $^{31}P\ \{^1H\}$ NMR data afford further significant structural information. There are two resonance doublets, at -146 and -164 ppm (PO_4H_3), with a PP coupling constant of 327 Hz. This value falls in the range for simple P–P bonds, whereas as the $^1J(PP)$ constants for P=P bonds are about 500–600 Hz [3].

The data suggest that in complex **2** there is side-on coordination of diphenyldiphosphene to the $[Cp_2TaH]$ moiety, with the classical canonical forms:



The diphosphene configuration in the complex is uncertain, and an X-ray diffraction study is necessary to establish it. In most of the previously described structures, the diphosphene ligand is in a *trans* configuration [4], but there are some examples with the diphosphene ligand in a *cis* configuration [5]. Such a geometry could account for the large anisochrony ($\Delta\nu \simeq 15$ Hz) observed for the Cp ligands in the complex **2**.

The mechanism of formation of $Cp_2Ta(H)(PPh)_2$ is unknown, but it can be assumed that in a preliminary step the dihydride $Cp_2Ta(H_2)PPh_2$ is formed by insertion of the fragment $[Cp_2TaH]$ into the Ph_2P–H bond. We have been able to synthesize the dihydride independently [6] and have observed that it is readily converted into **2** by heating with Ph_2PH. Complete identification of the various intermediates in the reaction is the subject of further study now in progress.

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References

1 (a) M. Yoshifugi, I. Sima, N. Inamoto, K. Hirotsu and P. Higuchi, J. Am. Chem. Soc., 103 (1981) 4587; (b) B. Cetinkaya, P.B. Hitchock, M.F. Lappert, A.J. Thorne and H. Goldwhite, J. Chem. Soc. Chem. Comm., (1982) 691; (c) C. Couret, J. Escudié, H. Ranaivonjatovo and J. Satgé, Organometallics, 5 (1986) 113.
2 A.H. Cowley, J.E. Kilduff, J.G. Lasch, N.C. Morman, M. Pakulski, E. Ando et T.C. Wright, Organometallics, 3 (1984) 1044.
3 (a) A.H. Cowley, J.E. Kilduff, M. Pakulski and C.A. Stewart, J. Am. Chem. Soc., 105 (1983) 1655; (b) C.A. McAuliffe, Comprehensive coordination chemistry, Pergamon, Oxford, 1987, vol. 2, p. 1045 and ref. therein.
4 (a) J.C. Green, M.L.H. Green and G.E. Morris, J. Chem. Soc. Chem. Comm., (1982) 932; (b) J. Chatt, P.H. Hitchock, A. Pidcock, C.P. Warrens and K.R. Dixon, ibid., (1982) 932; (c) P.S. Elms, P. Leverett and B.O. West, ibid., (1971) 747; B. Deppisch and H. Schafer, Acta Crystallogr. B, 38 (1982) 748.
5 (a) M.M. Olmstead and P.P. Power, J. Am. Chem. Soc., 106 (1984) 1495; (b) H. Vahrenkamp and D. Wolters, Angew. Chem. Int. Ed. Engl., 22 (1983) 154.
6 O. Lavastre, G. Bonnet, J.C. Leblanc and C. Moïse, unpublished results.