Isolable Paramagnetic Hydride Complexes of Niobium(IV) and Tantalum(IV)

Melvin L. Luetkens, Jr.,[a] **Wendy L. Elcesser,**[a] **John C. Huffman,**[b] **and Alfred P. Sattelberger***[a]

[a] *Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109, U.S.A.*
[b] *Molecular Structure Center, Indiana University, Bloomington, Indiana 47405, U.S.A.*

The paramagnetic hydride complexes, $(dmpe)_2MCl_2H_2$ [M = Nb, Ta; dmpe = 1,2-bis(dimethylphosphino)-ethane] have been isolated from the reactions of $(dmpe)_2MCl_2$ with molecular hydrogen and characterized by magnetic susceptibility measurements, i.r. and e.s.r. spectroscopy, and for the case where M = Ta, by *X*-ray crystallography.

Paramagnetic transition metal hydride complexes are very rare[1] and, in most cases, have been characterized in solution at low temperatures by e.s.r. spectroscopy or electrochemical techniques because they are thermodynamically unstable with respect to disproportionation,[2] reductive elimination,[3] or dimerization[4] at ambient temperature. The latter feature has necessarily frustrated any thorough investigation of the physicochemical properties, structural chemistry, and reactivity of these interesting inorganic radicals. Here we report an efficient and straightforward route to isolable, 17-electron hydride complexes of niobium(IV) and tantalum(IV) and describe some of their properties.

Reduction of $(dmpe)_2MCl_4$ (M = Nb,[5] Ta;[6] dmpe = $Me_2PCH_2CH_2PMe_2$) with 2 equiv. of sodium amalgam in

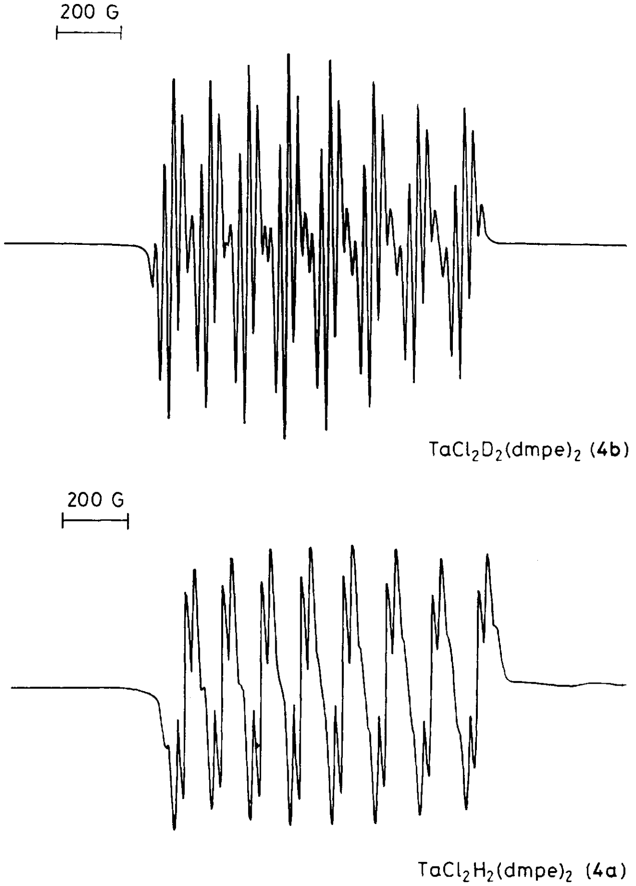

Figure 1. Room temperature e.s.r. spectra of (**4a**) and (**4b**) (in $PhCH_3$).

tetrahydrofuran (THF) provides high yields (*ca.* 90%) of the niobium(II) and tantalum(II) monomers, $(dmpe)_2MCl_2$ [equation (1)]. The tantalum(II) complex, (**2**), has been reported previously[6] but $(dmpe)_2NbCl_2$, (**1**), is a new compound.† It is, in fact, the first co-ordination complex of niobium(II) ever reported. Both of these dmpe derivatives are very air-sensitive in the solid state but are otherwise thermally stable, sublimable, brown crystalline solids which are soluble in hexane, toluene, and diethyl ether.

$$(dmpe)_2MCl_4 + 2\ Na\text{-}Hg \xrightarrow{THF} (dmpe)_2MCl_2 + 2\ NaCl \quad (1)$$

(**1**), M = Nb
(**2**), M = Ta

Hexane solutions of (**1**) or (**2**) react readily with hydrogen or deuterium (40 lb in^{-2}, 25 °C, 2 h) and deposit sparingly soluble red-orange precipitates [equation (2)]. The latter can be recrystallized from toluene–hexane at −40 °C in >80% yield. The new compounds are moderately air-sensitive in the solid state and decompose, without melting, at 145 (**3a**) and 190 °C (**4a**) in sealed evacuated capillaries. In addition to elemental analyses, the hydrides were characterized as follows. (i) Both (**3a**) and (**4a**) have room temperature magnetic moments (1.72 and 1.73 μ_B, respectively, by the Guoy method and including the diamagnetic correction) which are indicative of d^1 complexes with orbitally non-degenerate ground states. (ii) The i.r. spectra of (**3a**) and (**4a**) (Nujol mulls) show strong terminal M–H stretching modes at 1610 and 1650 cm^{-1}, respectively. These bands are absent in the i.r. spectra of (**3b**) and (**4b**) and are replaced by new bands (ν_{M-D}) at 1150 and 1185 cm^{-1}, respectively. (iii) Complexes (**3a, b**) and (**4a, b**) give good e.s.r. spectra in fluid solution at 25 °C. In Figure 1, we present the X-band spectra obtained for dilute toluene solutions of (**4b**) and (**4a**). An octet (^{181}Ta, $I = 7/2$, 100% abundance) of quintets is observed in both spectra: $\langle g \rangle = 1.97$, $\langle a \rangle_{Ta} = 126.0$ G, $\langle a \rangle_P = 25.8$ G. Although hydride coupling was not resolved in the e.s.r. spectrum of (**4a**) we estimate $\langle a \rangle_H$ to be *ca.* 6.0 G from the increase in line width [(**4b**) → (**4a**)] and computer simulations of the experimental spectra. A similar analysis of the spectra of (**3a**) and (**3b**) provided the following data: $\langle g \rangle = 1.96$, $\langle a \rangle_{Nb} = 109.0$ G, $\langle a \rangle_P = 25.5$ G, $\langle a \rangle_H = 11.1$ G.

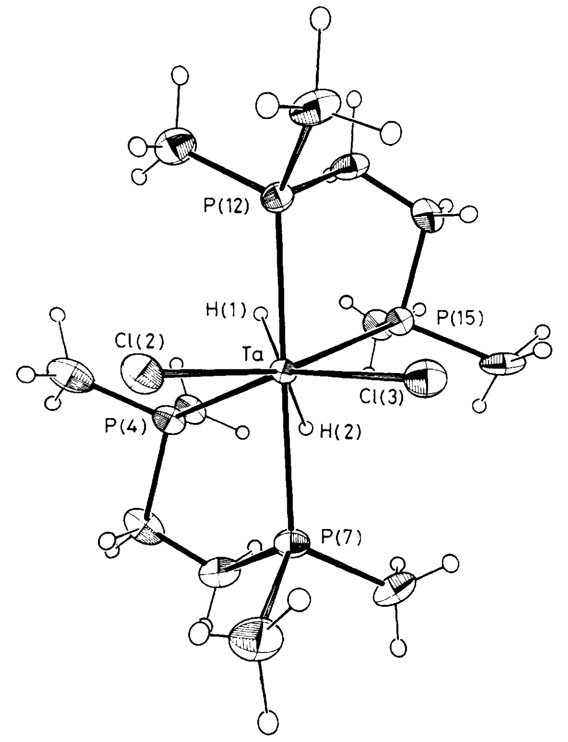

Figure 2. ORTEP drawing of $(dmpe)_2TaCl_2H_2$ (**4a**). Selected structural data: Ta–Cl(2), 2.546(3); Ta–Cl(3), 2.557(3); Ta–P(4), 2.523(3); Ta–P(7), 2.577(3); Ta–P(12), 2.564(3); Ta–P(15), 2.512(3) Å; Cl(2)–Ta–Cl(3), 85.0(1); P(4)–Ta–P(15), 121.1(1); P(7)–Ta–P(12), 162.2(1)°.

$$(dmpe)_2MCl_2 + X_2 \xrightarrow{C_6H_{14}} (dmpe)_2MCl_2X_2 \quad (2)$$

(**3**) **a**; M = Nb, X = H
b; M = Nb, X = D

(**4**) **a**; M = Ta, X = H
b; M = Ta, X = D

---

† The new compounds [*i.e.*, (**1**), (**3**), and (**4**)] gave acceptable C, H, and Cl microanalyses and parent ions were observed in the mass spectra of (**1**) and (**4**).

(iv) The *X*-ray structure of (**4a**) has been determined‡ and an ORTEP drawing of the molecule is shown in Figure 2. The terminal hydride ligands were located directly from difference Fourier maps and were well behaved during least-squares refinement: Ta–H(1), 1.94(10); Ta–H(2), 1.71(10) Å; H(1)–Ta–H(2), 74(4)°. Complex (**4a**) has virtual, but not crystallographically imposed, C_2 symmetry and is best described as a distorted square antiprismatic complex.[7] A list of selected structural data is provided in the caption to Figure 2. Note that (**4a**) contains chemically non-equivalent phosphorus atoms {*i.e.*, [P(4), P(15)] and [P(7), P(12)]}. This structural feature is not easily reconcilable with the binomial ^{31}P quintets observed in the solution e.s.r. spectra unless there is a fluxional process which renders the phosphorus nuclei equivalent on the e.s.r. time scale.[8]

We thank the National Science Foundation for support and the Wrubel Computing Center, Indiana University for a generous gift of computing time.

Received, 10th June 1983; Com. 772

---

‡ *Crystal data:* (**4a**), $C_{12}H_{34}P_4Cl_2Ta$, $M = 554.15$, orthorhombic, $a = 9.781(4)$, $b = 15.842(8)$, $c = 13.832(6)$ Å, $U = 2143.3$ Å^3, space group $P2_12_12_1$, $Z = 4$, $D_c = 1.717$ g cm^{-3}, μ(Mo-K_α) = 56.05 cm^{-1}.

Diffraction data were collected at -163 ± 2 °C using a θ–2θ scan technique. Data were corrected for absorption and the structure solved by Patterson and Fourier techniques. All atoms, including the terminal hydrides, were located and the positional and thermal parameters (anisotropic for Ta, Cl, P, and C; isotropic for H) refined. The atomic co-ordinates reported (*vide infra*) are for the proper enantiomorph for the crystal chosen, based on residuals for both settings. The final discrepancy indices were $R = 3.58$ and $R_w = 3.66\%$ for the 2000 independent reflections with $F_o \geqslant 2.33\sigma(F_o)$. The limits of data collection were $6° < 2\theta < 45°$.

The atomic co-ordinates for this work are available 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.

References

1 L. F. Rhodes, J. D. Zubkowski, K. Folting, J. C. Huffman, and K. G. Caulton, *Inorg. Chem.*, 1982, **21**, 4185, and references therein.

2 J. A. Labinger and K. S. Wong, *J. Organomet. Chem.*, 1979, **170**, 373.

3 I. H. Elson and J. K. Kochi, *J. Am. Chem. Soc.*, 1975, **97**, 1262.

4 R. J. Klingler, Jr., and J. K. Kochi, *J. Am. Chem. Soc.*, 1980, **102**, 208.

5 L. E. Manzer, *Inorg. Chem.*, 1977, **16**, 525.

6 S. Datta and S. S. Wreford, *Inorg. Chem.*, 1977, **16**, 1134.

7 S. J. Lippard and B. J. Russ, *Inorg. Chem.*, 1967, **6**, 1943.

8 Stereochemical nonrigidity is a pervasive feature of the chemistry of eight co-ordinate complexes. See: J. Burdett, R. Hoffmann, and R. C. Fay, *Inorg. Chem.*, 1978, **17**, 2553, and references therein.