

Priority communication

Phosphorus ylide niobium complexes; synthesis and characterization of the first α -keto ylide complexes, $[\{\text{NbCl}_3(\text{ylide-O,N})\}_2]$ and $[\text{NbCl}_3(\text{ylide-O,N})(\text{RC}\equiv\text{CR}')]$ (ylide = $[\{2\text{-thiazolylcarbonyl}\}\text{methylene}\}\text{triphenylphosphorane}$, $\text{NOSC}_4\text{H}_2\text{CH-PPH}_3$). Molecular structure of $[\text{NbCl}_3(\text{NOSC}_4\text{H}_2\text{CHPPH}_3\text{-O,N})(\text{PhC}\equiv\text{CPr})]$ (Ph = phenyl, Pr = propyl)

E. Diez-Barra ^a, J. Fernández-Baeza ^a, M.M. Kubicki ^b, A. Lara-Sánchez ^a, A. Otero ^{a,*}, N. Poujaud ^b, J. Tejada ^a

^a *Departamento de Química Inorgánica, Orgánica y Bioquímica, Facultad de Ciencias Químicas, Universidad de Castilla-La Mancha, Campus Universitario, 13071 Ciudad Real, Spain*

^b *Laboratoire de Synthèse et d'Electrosynthèse Organométalliques, CNRS URA 1685, Faculté des Sciences Gabriel, 6 bd. Gabriel, 21000 Dijon, France*

Received 3 December 1996

Abstract

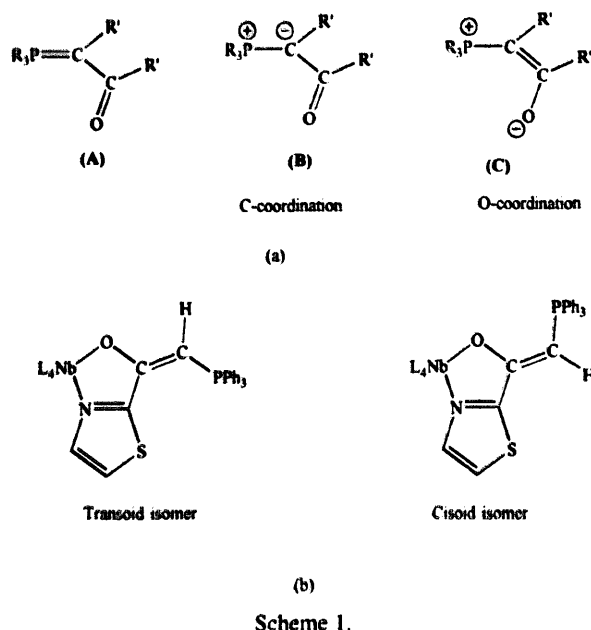
Reactions of $[\{\text{NbCl}_3(\text{dme})\}_n]$ or $[\text{NbCl}_3(\text{dme})(\text{RC}\equiv\text{CR}')]$ with a heterocycle containing α -keto stabilized phosphorus ylide, 2-TCMP = $[\{2\text{-thiazolylcarbonyl}\}\text{methylene}\}\text{triphenylphosphorane}$, allowed the synthesis of the first α -keto ylide niobium complexes, $[\{\text{NbCl}_3(2\text{-TCMP})\}_2]$ and $[\text{NbCl}_3(2\text{-TCMP})(\text{RC}\equiv\text{CR}')]$ respectively. The new complexes were spectroscopically characterized and the X-ray molecular structure for one of them was also determined. © 1997 Elsevier Science S.A.

Phosphorus ylides constitute an important class of compound in the field of organometallic chemistry, mainly due to their interesting applications in metal-promoted organic syntheses [1]. The chemistry of early transition metals and ylides is mainly limited to cyclopentadienyl complexes and ylides of the type $\text{R}_3\text{P}=\text{CR}'\text{R}''$ (for selected examples see Ref. [2]). In this context there are only a few known examples [3] of complexes of early transition metals with α -keto stabilized phosphorus ylides $\text{R}_3\text{P}=\text{C}(\text{R}')\text{COR}''$, which may act as ambidentate ligands (C vs. O coordination) due to the potential resonance forms A–C (Scheme 1(a)). With these precedents we initiated a study of the reactivity of a heterocycle containing α -keto ylide, $[\{2\text{-thiazolylcarbonyl}\}\text{methylene}\}\text{triphenylphosphorane}$ $\text{NOSC}_4\text{H}_2\text{-CHPPH}_3=2\text{-TCMP}$, which can potentially act as a

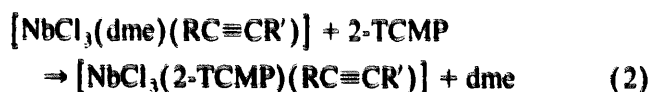
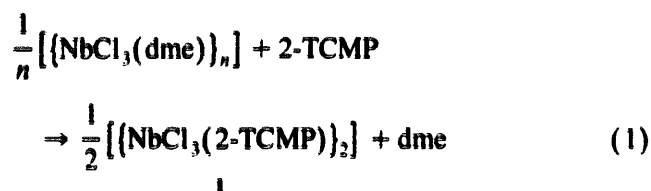
chelating ligand towards Nb(III) complexes $[\{\text{NbCl}_3(\text{dme})\}_n]$ and $[\text{NbCl}_3(\text{dme})(\text{RC}\equiv\text{CR}')]$ (dme = 1,2-dimethoxyethane). [To date, only one ylide containing niobium complex, from the reaction of $\text{CpNb}(\text{N}^i\text{Bu})\text{Cl}_2$, $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, and $\text{Ph}_3\text{P}=\text{CH}_2$, has been described [4]]. We report here the synthesis and structural characterization of the first α -keto ylide niobium complexes and indeed the first example of this class of ligand acting in a chelating manner, in this case through N,O-coordination to the metal center (monodentate O-bound transition metal–ylide complexes are scarce, see Refs. [3,5–7]).

Complexes 1 and 2–8 were formed by reacting the ligand 2-TCMP (prepared from a modification to a previously described method [8]; the yield of the process was clearly improved and the ylide compound was spectroscopically fully characterized) with the starting materials $[\{\text{NbCl}_3(\text{dme})\}_n]$ and $[\text{NbCl}_3(\text{dme})(\text{RC}\equiv\text{CR}')]$ respectively. The products were isolated in good yields

* Corresponding author.



after appropriate work-up, as air-sensitive green-brown ¹ and orange-brown ² solids (Eqs. (1) and (2)):



¹ Complex **1** was obtained as a green-brown solid by the reaction of $[\text{NbCl}_3(\text{dme})]_n$ (240 mg, 0.820 mmol) with 2-TCMP (321 mg, 0.820 mmol) in THF (20 cm³) at room temperature for 20 h (yield 80%). ¹H NMR (CDCl₃): δ 5.40 (d, CH), 8.20 (d, H_b), 7.60 (d, H_c). ¹³C-(¹H) NMR (CDCl₃): δ 71.50 (d, CH), 144.30 (s, CO), 168.30 (s, C_a), 142.80 (s, C_b), 124.40 (s, C_c). ³¹P-(¹H) NMR (CDCl₃, H₃PO₄ as reference): δ 18.88 (s, PPh₃). IR (Nujol): 1553 [ν(C=O)], 379, 334, 313 and 291 cm⁻¹ [ν(Nb-Cl)]. Anal. Found: C, 46.7; H, 3.2; N, 2.5. C₄₆H₁₆Nb₃Cl₆N₂O₂P₂S₂. Calc.: C, 47.0; H, 3.1; N, 2.3%. Mass spectrum: *m/z* 1175D (M+1).

² Complex **7** was obtained as a brown solid by the reaction of $[\text{NbCl}_3(\text{dme})(\text{PhC}\equiv\text{CPr})]$ (174 mg, 0.400 mmol) with 2-TCMP (155 mg, 0.400 mmol) in THF (20 cm³) at room temperature for 20 h (yield 86%). A single crystal suitable for study by X-ray diffraction was obtained from CH₂Cl₂/Et₂O. ¹H NMR (CDCl₃): δ 5.10 (d, CH), 8.57 (d, H_b), 7.57 (d, H_c). ¹³C-(¹H) NMR (CDCl₃): δ 71.53 (d, CH), 165.20 (s, CO), 171.00 (s, C_a), 142.80 (s, C_b), 123.20 (s, C_c). ³¹P-(¹H) NMR (CDCl₃, H₃PO₄ as reference): δ 18.95 (s, PPh₃). IR (Nujol): 1556 [ν(C=O)], 1692 [ν(C≡C)], 378 and 311 cm⁻¹ [ν(Nb-Cl)]. Anal. Found: C, 55.4; H, 4.7; N, 2.1. C₃₄H₁₆NbCl₃NOPS. Calc.: C, 55.8; H, 4.2; N, 1.9%.

R = R' = Ph (**2**); R = R' = Me (**3**); R = R' = Et (**4**);
R = Ph, R' = Me (**5**); R = Ph, R' = Et (**6**);
R = Ph, R' = Pr (**7**); R = Ph, R' = SiMe₃ (**8**)

Complexes **3**, **4** and **6** were obtained from the corresponding reaction as a mixture with compound **1**, resulting from the loss of the corresponding coordinated alkyne. They could, however, be isolated as pure compounds by recrystallization. Spectroscopic techniques proved useful for the characterization of the different complexes and allowed us to distinguish between O-coordination and C(methine)-coordination of the ylide ligand. The ¹H, ¹³C and ³¹P NMR spectra indicated that the 2-TCMP ligand is bound through the carbonyl oxygen. The ²J(³¹P-¹H) values for the methine proton interaction with the phosphorus and the ¹J(³¹P-¹³C) values for P=C(methine) are smaller in the complexes than in the free ylide, for example for **2** they are 15.0 and 105.3 Hz while for the free ylide they are 23.0 and 111.0 Hz respectively, and are in accordance with the known coupling constant trend free ylide > O-coordinated ylide > ylide hydrohalide salt > C-coordinated ylide [3,6]. ³¹P NMR resonances were observed to occur at a slightly lower field with respect to the free ylide. IR spectroscopy has previously been demonstrated to be another reliable indicator of the bonding mode of α-keto ylides [3,5–7]. Bonding through the carbonyl oxygen (where C in Scheme 1(a) is the major resonance contributor) leads to a decrease in the carbonyl stretching frequency. However, in complexes **1–8** the ν(CO) appears at slightly higher values than in the free ylide. This situation, which is surprising, may be justified by considering the structure of the complexes. In compounds **1–8**, the α-keto ylide ligand behaves as a chelate through N,O-coordination (vide infra) to give five-membered metallacycles in which the

O-atom is proposed to be sp^2 hybridized, thus probably favoring effective π -bonding with the C(methine) atom to give a strong C=O bond. An X-ray crystal study (vide infra) supports this proposal. The spectroscopic data indicate also the presence of only one of the two possible isomers, cisoid and transoid, in each of these O-coordination, Group 5 ylide complexes (Scheme 1(b)). The cisoid isomer, which would appear to be favored on steric arguments in our complexes, has been proposed to be present both in solution and in the solid state (vide infra). A mass spectrum of **1** showed it to be a binuclear complex, and from the spectroscopic data a complex in which each of the niobium atoms has the terminal chloride ligands trans in an octahedral environment and the O,N atoms of the ylide ligand occupying equatorial coordination sites was proposed (Fig. 1) (this structural geometry has been described in analogous binuclear complexes with both terminal and bridging halide ligands [9]). The IR spectra of complexes **2–8** show in addition absorptions at ca. 1680 cm^{-1} which correspond to the $\nu(\text{C}\equiv\text{C})$ mode of the coordinated alkynes. The ^{13}C NMR spectra show resonances at ca. 240 ppm for the alkyne carbons indicating that this class of ligand in complexes **2–8** behaves as a four-electron donor [10]. Variable temperature NMR studies show the alkyne ligand in these complexes to be static. (This behavior contrasts with that previously described for other poly(pyrazol-1-yl)methane containing niobium(III) complexes; see Ref. [11].) Assuming a six-coordinate description of the complexes in which the alkyne occupies a single site, a structure in which this is located perpendicular to the equatorial plane defined by the N, O, Cl and Nb atoms is proposed. In order to confirm this proposal as well as the coordination mode of the ylide ligand, an X-ray crystal structure determination for **7** was carried out, and an ORTEP drawing is shown in Fig. 2¹.

The structure of **7** is built up of discrete molecules in

¹ Crystal data for complex **7**: $\text{C}_{34}\text{H}_{30}\text{NbCl}_3\text{NOP}$, $M = 790.93$, triclinic, space group $P\bar{1}$, $a = 8.900(2)$, $b = 12.502(2)$, $c = 16.178(3)\text{ \AA}$, $\alpha = 80.91(1)$, $\beta = 87.76(2)$, $\gamma = 69.85(2)^\circ$, $U = 1668.6(6)\text{ \AA}^3$, $Z = 2$, $\mu = 7.216\text{ cm}^{-1}$, $F(000) = 744$, $T = 296\text{ K}$. Intensity data (7134, $2\theta_{\text{max}} = 52^\circ$) were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073\text{ \AA}$), ψ -scan absorption convention applied. 3450 unique reflections with $I > 3\sigma(I)$ were used in the refinement. The structure was solved by the analysis of Patterson synthesis and refined by full-matrix least-squares on F_o to $R = 0.045$ and $R' = 0.047$; $w = [\sigma^2(I) + (0.04F_o)^2]^{-1/2}$. Computation used the Molen library [12] with neutral atom scattering factors. The n-Pr substituent of the alkyne ligand showed a disorder in the positions of CH_2 groups. Thus, the corresponding carbon atoms were refined with occupancies equal to 0.5. The hydrogen atoms were placed in calculated positions. Atomic coordinates, thermal parameters, best planes, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

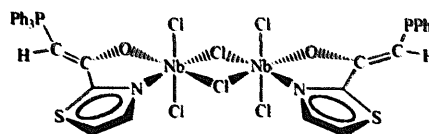


Fig. 1. Proposed structure for complex **1**.

which the central niobium atom is surrounded by an (O,N)-chelating ylide ligand, three chlorides and an η^2 -coordinated alkyne. The α -keto ylide adopts a cisoid geometry already observed in other O-bonded keto phosphorus ylides [3,7]. The entire ligand, Nb, O, N and Cl2 atoms, are roughly co-planar (within 0.07 \AA), indicating a large degree of electron density delocalization. Thus, the P–C5 distance ($1.755(5)\text{ \AA}$) is much longer than the formally P=C double bond in $\text{R}_3\text{P}=\text{CH}_2$ ylides ($\text{R} = \text{Me}$, 1.64 \AA , $\text{R} = \text{Ph}$, 1.66 \AA) [11,13]. This distance is intermediate between the values reported for other O-bonded keto ylides of titanium ($1.754(7)\text{ \AA}$) [3] and of palladium ($1.732(3)\text{ \AA}$) [7] and falls in the lower range of values observed for C-bound phosphorus ylides ($1.76\text{--}1.81\text{ \AA}$) [3,14]. The C4–O bond length of $1.289(7)\text{ \AA}$ corresponds well to the values found in Ti and Pd structures ($1.332(8)$ and $1.275(4)\text{ \AA}$), indicating the following increasing strength of the metal–oxygen bond and of the intraligand (P^+-O^-) polarization: $\text{Pd} < \text{Nb} < \text{Ti}$. The C4–C5 distance ($1.370(7)\text{ \AA}$) is once more close to those given for Ti and Pd complexes, all three being shorter than the corresponding C–C bond lengths in C-bound ylides.

The Nb–Cl2 (trans to oxygen) bond ($2.417(2)\text{ \AA}$) is shorter than the Nb–Cl1 and Nb–Cl3 ones ($2.437(2)$ and $2.444(3)\text{ \AA}$). All these distances correspond better to the Nb–terminal Cl observed in seven-coordinated niobium complexes than in the six-coordinated ones [15].

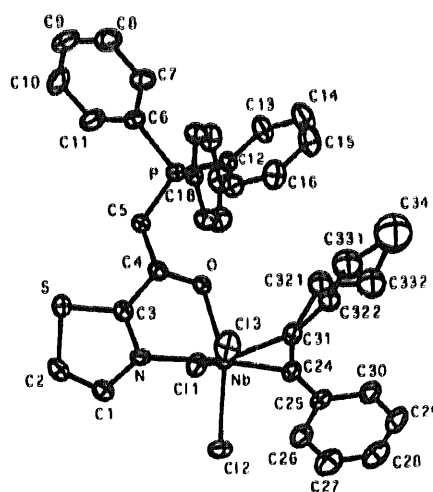


Fig. 2. ORTEP view (30% probability level) of **7**. A disorder of n-Pr alkyne substituent is shown. Selected bond distances (\AA) and angles ($^\circ$): Nb–O $2.148(3)$, Nb–N $2.344(5)$, C(24)–C(31) $1.288(9)$, Nb–C(24) $2.066(6)$, Nb–C(31) $2.026(6)$; and some angles: O–Nb–N $72.3(1)$, O–Nb–Cl(2) $159.0(1)$, Cl(1)–Nb–Cl(3) $161.28(6)$, C(24)–Nb–C(31) $36.7(2)$, O–C(4)–C(5) $125.4(5)$.

The Nb–O and Nb–N distances fall in the usual range for these bonds [15].

The dihedral angle between the ylide, Nb, O, N, C12 best plane and that of the Nb, C24, C31 (alkyne) plane is close to 43°, suggesting a lack of orbital control of the conformation of the C24–C31 alkyne bond. An interesting feature to be emphasized is the co-planarity of the O, C11, C12, C13 atoms (within 0.02 Å) with the Nb atom moving away by ~ 0.4 Å from this plane.

Studies on the reactivity of these complexes as well as the preparation and characterization of new complexes of Group 4 metals are now in progress.

Acknowledgements

The authors gratefully acknowledge financial support from the Dirección General de Investigación Científica y Técnica (Grant No. PB-92-0715) of Spain.

References

- [1] A.W. Johnson, W.C. Kaska, K.A.O. Starzewski, D.A. Dixon, *Ylides and Imines of Phosphorus*, Wiley, New York, 1993, Chap. 14 and references cited therein.
- [2] H. Schmidbaur, R. Pichl, G. Müller, *Angew. Chem.* 98 (1986) 572; W. Scharf, D. Neugebauer, U. Schubert, H. Schmidbaur, *Angew. Chem.* 90 (1978) 628; G. Erker, P. Czisch, R. Benn, A. Rufinska, R. Mynott, *J. Organomet. Chem.* 328 (1987) 101; G. Erker, P. Czisch, R. Mynott, Y.-H. Tsey, C. Kruger, *Organometallics* 4 (1985) 1310; G. Erker, K. Ergel, U. Korek, P. Czisch, H. Berke, P. Caubere, R. Vandesse, *Organometallics* 4 (1985) 1531; K.I. Gell, J. Schwartz, *Inorg. Chem.* 19 (1980) 3207; G. Erker, P. Czisch, R. Mynott, *J. Organomet. Chem.* 334 (1987) 91; G. Erker, P. Czisch, C. Kruger, J.M. Wallis, *Organometallics* 4 (1985) 2059.
- [3] J.A. Albanese, D.A. Staley, A.L. Rheingold, J.L. Burmeister, *Inorg. Chem.* 29 (1990) 2209.
- [4] S. Schmidt, J. Sundermeyer, F. Moller, *J. Organomet. Chem.* 475 (1994) 157.
- [5] J. Buckle, P.-G. Harrison, T.J. King, J.A. Richards, *J. Chem. Soc., Chem. Commun.* (1972) 1104; J. Buckle, P.G. Harrison, *J. Organomet. Chem.* 47 (1973) C17; I. Kawafune, G. Matsubayashi, *Inorg. Chim. Acta* 70 (1983) 1.
- [6] R. Usón, J. Forniés, R. Navarro, P. Espinet, C. Mendivil, *J. Organomet. Chem.* 290 (1985) 125.
- [7] L.R. Falvello, S. Fernández, R. Navarro, E.P. Urriolabeitia, *Inorg. Chem.* 35 (1996) 3064.
- [8] A. Dondoni, P. Marino, A.W. Douglas, I. Schinkai, *J. Am. Chem. Soc.* 116 (1994) 3324.
- [9] F.A. Cotton, L.R. Falvello, R.C. Najjar, *Inorg. Chem.* 22 (1983) 375.
- [10] J. Fernández-Baeza, F.A. Jalón, A. Otero, M.E. Rodrigo-Blanco, *J. Chem. Soc., Dalton Trans.* (1995) 1015; J.L. Templeton, *Adv. Organomet. Chem.* 29 (1989) 1.
- [11] E.A.V. Ebsworth, T.E. Fraser, D.W.H. Rankin, *Chem. Ber.* 110 (1977) 3494.
- [12] C.K. Fair, Molen, *An Interactive Structure Solution Procedure*, Enraf-Nonius, Delft, Netherlands, 1990.
- [13] H. Schmidbaur, J. Jeong, A. Schier, W. Graf, D.L. Wilkinson, G. Müller, C. Krüger, *New J. Chem.* 13 (1989) 341.
- [14] H. Scordia, R. Kergoat, M.M. Kubicki, J.E. Guerschais, *Organometallics* 2 (1983) 1681.
- [15] A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson, R. Taylor, *J. Chem. Soc., Dalton Trans.* (1989) S1.