Inorganica Chimica Acta, *202* (1992) 121–122

Inorganica Chimica Acta
LETTER

Bis(alkyne) complexes of niobium(I), containing the alkyne as a three-electron donating ligand

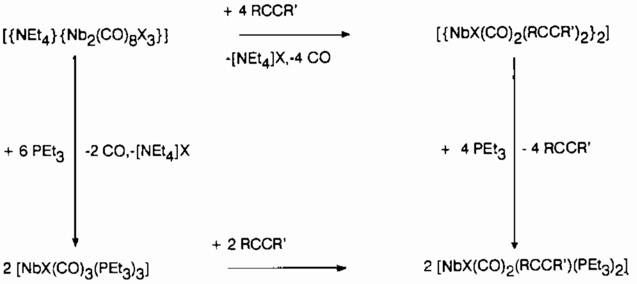
Christian Felten, Dieter Rehder*
Universität Hamburg, Institut für Anorganische und Angewandte Chemie, Martin Luther King Platz 6, W-2000 Hamburg 13 (Germany)

Guido Pampaloni and Fausto Calderazzo
Dipartimento di Chimica e Chimica Industriale, Sezione di Chimica Inorganica, Università di Pisa, via Risorgimento 35, I-56126 Pisa (Italy)

(Received June 30, 1992)

Bis(alkyne) complexes of the transition metals are assumed to be intermediates for transition metal catalyzed polymerization and oligomerization reactions. They have also been crucial to the development of a comprehensive model for π donation in d^4 transition metal complexes [1]. A feature of particular interest in complexes containing two equivalent alkynes is a formal donor number of three electrons for each alkyne.

The chemistry of alkyne complexes of low valent Group 5 metals is much less developed than of the metals in the adjacent chromium triade. While alkyne complexes of Mo^{II} and W^{II} have been known and thoroughly investigated for more than two decades [1], only a few accounts on the corresponding d^4 Nb^I and Ta^I compounds without supporting Cp ligands have so far appeared [2a–e], and none reporting on bis(alkyne) complexes. In a previous paper, we described monoalkyne complexes of Nb^I [2a] with the alkyne as a four-electron donating ligand; we have now synthesized and characterized dinuclear halide bridged bis(alkyne) compounds.



Scheme 1.

Reaction between stoichiometric amounts of alkynes RCCR′ (R = R′ = Me, Et, Ph; R = H, R′ = Ph) with the known [3] dinuclear halide bridged $[\{NEt_4\}\{Nb_2X_3(CO)_8\}]$ (X = Br or I) in tetrahydrofuran and at room temperature leads to moderate yields of pale yellow and very air sensitive neutral complexes of composition $[\{NbX(CO)_2(RCCR')_2\}_2]$ (X = Br, R = R′ = Ph (**1a**); X = I, R = R′ = Ph (**2a**); R = Ph, R′ = H (**2b**); R = R′ = Et (**2c**); R = R′ = Me (**2d**)).** The dimeric nature is supported by FAB mass spectra (glycerine matrix): while the dominant peaks are due to ions of the mononuclear species, weak peaks corresponding to dinuclear ions were observed in some cases. In order to avoid any partial excess of the alkyne in the reaction mixture and hence to minimize polymerization or cyclo-oligomerization, thf solutions of the alkynes are added to the starting material over a period of upto 48 h. Yields of products were around 50% and seemed to depend significantly on the purity of the precursor carbonylniobium complexes. Attempts failed to isolate a complex with the parent acetylene HCCH: only benzene (detected by GC and ^1H NMR) and silvery black flakes of a mixture of *cis*/*trans* polyacetylene (by IR spectroscopy) were isolated. Reactions of **2a** and **2c,d** with PEt_3 were carried out to assess the reactivity of the bis(alkyne) compounds towards nucleophiles. Addition of the phosphine in 1:1 ratio to thf solutions of **2** afforded rapid cleavage of the halide bridges and substitution of one of the alkynes resulting in deep raspberry red solutions of $[NbX(CO)_2RCCR'(PEt_3)_2]$ (see Scheme 1), prepared previously from $[NbX(CO)_3(PEt_3)_3]$ [2a].

Assuming dimers with bridging halides, several structural isomers (see Fig. 1) are possible for the complexes

---

*Author to whom correspondence should be addressed.

All new compounds gave satisfactory elemental analyses. Selected spectroscopic data (^1H NMR at 360 MHz and $^{13}C\{^1H\}$ NMR at 145.8 MHz in $[^2H_8]$thf, δ in ppm relative to Me_4Si; IR in thf, 0.1 mm CaF_2, ν (cm^{-1})): **1a: IR, 2071w, 2031vs (CO), 1708w (CC); ^1H NMR, 7.35 (m, PhCCPh); ^{13}C NMR, 223.7 (CO), 183.9, 178.3 (CC), 132.3 (m, phenyl carbons). **2a**: IR, 2062w, 2013vs (CO), 1712w (CC); ^1H NMR, 7.35 (m, PhCCPh); ^{13}C NMR, 225.9 (CO), 183.2, 179.8 (CC) 130.6 (m, phenyl carbons). **2b**: 2002vs (CO), 1750w (CC); ^1H NMR, 9.86, 9.63 (C*H*), 7.22 (m, 20H, Ph). **2c**: IR, 1965w, 1939vs (CO), 1761w (CC); ^1H NMR, 3.47, 3.06 (CH_2), 2.89, 2.29 (CH_3); ^{13}C NMR, 233.5 (CO), 173.2, 165.0 (CC), 31.0 (CH_2), 15.8 (CH_3). **2d**: IR, 1945w, 1930s (CO), 1772w (CC), ^1H NMR, 2.66, 2.42 (CH_3); ^{13}C NMR, 232.6 (CO), 173.2, 165.0 (CC), 21.3, 16.6 (CH_3).

0020-1693/92/$5.00

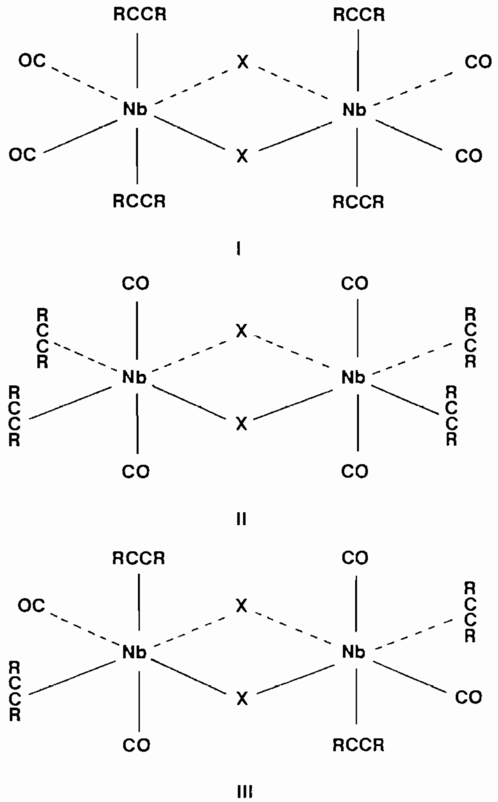


Fig. 1. Structural isomers for bis(alkyne) complexes of the type $[\{NbX(CO)_2(RCCR)_2\}_2]$.

TABLE 1. ^{13}C chemical shifts of alkyne carbons bound to d^4 metals

Compound	$\delta(CC)$	N[a]	Reference
$[TaI(CO)_2(PhCCPh)(PMe_3)_2]$	209.2	4	2c
$[NbI(CO)_2(EtCCEt)(PEt_3)_2]$	209.0	4	2a
$[\{NbBr(CO)_2(PhCCPh)_2\}_2]$	183.2/179.9	3	[b]
$[\{NbI(CO)_2(PhCCPh)_2\}_2]$	183.9/178.3	3	[b]
$[\{NbI(CO)_2(EtCCEt)_2\}_2]$	177.2/168.7	3	[b]
$[\{NbI(CO)_2(MeCCMe)_2\}_2]$	173.2/165.0	3	[b]
$[\{WBr_2CO(MeCCMe)_2\}_2]$	179.8/162.6	3	7
$[C_5Me_5Nb(CO)(MeCCMe)_2]$	167.8/164.7	3	8
$[(C_5H_5)_2Mo(MeCCMe)]$	115.2	2	6

[a] N = no. of electrons formally donated by each alkyne to the metal. [b] This work.

1a and **2a–d**. The spectroscopic data available do not allow for an unambiguous structure assignment. The presence of only one ^{13}C NMR signal in the CO region favours structures I and II, while the intensity ratio of the $\nu(CO)$ bands supports a *trans* position of the carbonyls as in II. On the other hand, the presence of 2 sets of ^1H and ^{13}C NMR signals for the alkyne ligands should account for structure III. The $\nu(CC)$ (alkyne) stretching bands are shifted to lower wave numbers by upto 400 cm^{-1} in the complexes relative to the uncoordinated alkynes.

The favoured 18-electron configuration of the complexes **1a** and **2a–d** in the absence of a metal–metal double bond is attained with the alkyne ligands acting as three-electron donors, a view which is strongly supported by ^{13}C NMR studies. According to Templeton and Ward [4] and Allen *et al.* [5], the number of electrons donated by an alkyne ligand is correlated to the ^{13}C NMR chemical shifts of the coordinated alkyne carbons. Involvement of both sets of π orbitals of the alkyne in bonding to the metal leads to a pronounced high frequency shift of the ^{13}C NMR resonances. Thus, four-electron donation, as in the monoalkyne derivatives $[NbX(CO)_2(RCCR')(PEt_3)_2]$ yields values >200 ppm [2a]. The bis(alkyne) complexes **1a** and **2a,c,d**, where three-electron donation is expected, exhibit two resonances in the range $\delta = 164–185$ ppm. Typical δ values for two-electron donation such as in $[(C_5H_5)_2Mo(MeCCMe)]$ [6] are around 110–120 ppm (see also Table 1 for selected examples). In the ^1H NMR spectrum, the CH moiety of the alkyne in $[\{NbX(CO)_2(PhCCH)_2\}_2]$ displays low field signals at $\delta = 9.63$ and 9.86, again indicating three-electron donation in accordance with findings for other bis(alkyne) complexes of d^4 metals.

Acknowledgements

The authors gratefully acknowledge the financial support by the Deutscher Akademischer Austausch Dienst (DAAD) and the Ministero dell'Università e della Ricerca Scientifica e Tecnologia (MURST).

References

1 J. L. Templeton, *Adv. Organomet. Chem., 29* (1989) 1.
2 (a) F. Calderazzo, Ch. Felten, G. Pampaloni and D. Rehder, *J. Chem. Soc., Dalton Trans.,* (1992) 2003; (b) R. N. Vrtis, S. Liu, C. Pulla Rao, S. G. Bott and S. J. Lippard, *Organometallics, 10* (1991) 275; (c) M. J. McGeary, A. S. Gamble and J. L. Templeton, *Organometallics, 7* (1988) 271; (d) P. A. Bianconi, I. D. Williams, M. P. Engeler and S. J. Lippard, *J. Am. Chem. Soc., 108* (1986) 311; (e) P. A. Bianconi, R. N. Vrtis, C. Pulla Rao, I. D. Williams and M. P. Engeler, *Organometallics, 6* (1987) 1968.
3 F. Calderazzo and G. Pampaloni, *J. Chem. Soc., Chem. Commun.,* (1984) 1249.
4 J. L. Templeton and B. C. Ward, *J. Am. Chem. Soc., 102* (1980) 2188.
5 S. R. Allen, P. K. Baker, S. G. Barnes, M. Green, L. Trollope, Lj. Manojlovic-Muir and K. W. Muir, *J. Chem. Soc., Dalton Trans.,* (1981) 873.
6 J. L. Templeton and B. C. Ward, *J. Am. Chem. Soc., 102* (1980) 3288.
7 L. Davidson and G. Vasapollo, *J. Chem. Soc., Dalton Trans.,* (1985) 2239.
8 H. G. Alt and H. E. Engelhardt, *Z. Naturforsch., Teil B, 42* (1987) 711.