Interpretation of Bond-length Data for Transition-metal–Acetylene Complexes, in Particular the Complex $[C_5H_5NH][TaCl_4(PhC{\equiv}CPh)(NC_5H_5)]$ *

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By analogy with cyclopropene, a simple metallocene model for transition-metal–acetylene complexes should be described as containing bent bonds. On the basis of this model, a simple method for predicting metal–carbon and carbon–carbon distances is proposed and its application to $[C_5H_5NH][TaCl_4(PhC{\equiv}CPh)(NC_5H_5)]$ is described in detail. It is concluded that the reported structural data for this compound are fully consistent with those expected for a simple bent-bond model, and that there is no compulsion on the basis of bond-length data to invoke a contribution to bonding from four-electron donation from the acetylene to the metal, as was previously proposed.

RECENTLY, Cotton and Hall[1] reported the crystal structure of the complex $[C_5H_5NH][TaCl_4(PhC{\equiv}CPh)(NC_5H_5)]$. The observed geometry of the ligands around Ta is distorted octahedral if the acetylene is considered as a unit. On the other hand, the co-ordination number may be taken as seven, with an approximately monocapped trigonal-prismatic 2,4,1 arrangement of two carbon atoms, four Cl atoms, and the nitrogen atom of the pyridine. The principal features of the structure are shown in Figure 1. The Ta atom is reported to be displaced 0.38 Å out of the plane of the Cl atoms towards the acetylene and the co-ordinated pyridine to be only 9.3° from coplanarity with the TaCC ring.

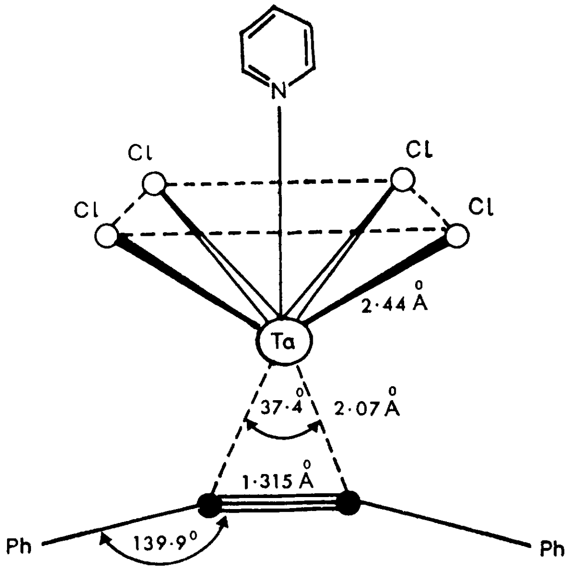
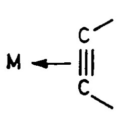
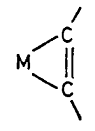


FIGURE 1 The principal structural parameters of Cotton's tantalum complex, $[TaCl_4(PhC{\equiv}CPh)(NC_5H_5)]^-$

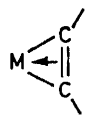
The authors comment that the most remarkable feature of the structure is the bonding of the Ta atom to the acetylene, which is very strong and symmetrical. They conclude that a simple μ-bond representation, (I), or a metallocene representation, (II), with two single Ta–C bonds, do not adequately account for the structure and they, therefore, consider contributions from structures such as (III). Such a contribution increases the electron configuration of the metal from formally 14 to 16 electrons. The rather short Ta–C distances in the complex, close to 2.0 Å, were used to support this argument, and were compared, for example, to the formal Ta=C bond length of 2.07(1) Å found in the complex $[Ta(CHPh)(CH_2Ph)(C_5H_5)_2]$.[2]



(I)



(II)



(III)

I now suggest an alternative approach to the description of bonding in metal–acetylene compounds, based on a recent development[3] of Pauling's bent-bond model.[4] In this model a double bond is depicted as formed from the overlap of two sp^3 hybrid orbitals on each carbon atom, and a triple bond from the overlap of three such orbitals. As Pople[5] has noted, these models are equivalent to the better known σ–π descriptions. They predict not only the shortening of both single and double C–C bonds in cyclopropane and cyclopropene but also the ' bend-back ' angles H–C=C in cyclopropene.[3]

RESULTS AND DISCUSSION

If we assume the three-centre bond between a metal and an acetylene to be analogous to that in cyclopropene, with the metal atom replacing the CH_2 group, the geometric relations between bond lengths and angles can be calculated from Figure 2. The C=C bond, with the normal double-bond length of r_2, is represented here as an arc of constant curvature, α is defined as the angle between the tangent to this arc and the C–C axis, and β as the angle between the same tangent and the C–X bond. The apparent (linear) C–C bond length r is given by equation (1). In order to compare the observable parameters,

$$r/r_2 = (360/2\pi)(\sin\alpha)/\alpha \qquad (1)$$

r, and the bend-back angle, $\theta = (\beta + \alpha)$, with the results calculated from this model, for simplicity, either

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* Pyridinium tetrachloro(diphenylethyne)pyridinetantalate.

TABLE 1

Observed bend-back angles, θ, and CC bond lengths, r_2, in some acetylene complexes

Complex	$\theta_{obs.}/°$	$r_{obs.}/Å$	$r_{calc.}/Å$		Ref.
			a	*b*	
(1) $[PtMe(MeC{\equiv}CMe)(PMe_2Ph)_2]^+$	168(4)	1.22(3)	1.20	1.20	*c*
(2) $[PtCl_2(Bu^tC{\equiv}CBu^t)(NH_2C_6H_4Me)]$	164(2)	1.235(18)	1.22	1.23	*d*
(3) $[Pt(PhC{\equiv}CPh)_2]$	153	1.280(6)	1.27	1.27	*e*
(4) $[Pt(PhC{\equiv}CPh)_2(PMe_3)_2]$	153	1.26(5)	1.27	1.27	*e*
(5) $[Ni(PhC{\equiv}CPh)(NCBu^t)_2]$	149(1)	1.284(16)	1.28	1.29	*f*
(6) $[PtMe(htpb)(F_3CC{\equiv}CCF_3)]$ [g]	146(4)	1.292(12)	1.29	1.30	*h*
(7) $[WPh(C_5H_5)O(PhC{\equiv}CPh)]$	144(4)	1.29(3)	1.29	1.30	*i*
(8) $[PtMe(Cl)(AsMe_3)_2(F_3CC{\equiv}CCF_3)]$	143	1.32(4)	1.30	1.31	*j*
(9) $[Fe(CO)_4(Bu^tC{\equiv}CBu^t)]$	143	1.283	1.30	1.31	*k*
(10) $[Nb(C_5H_5)(CO)(C_4Ph_4)(PhC{\equiv}CPh)]$	142	1.26(4)	1.30	1.31	*l*
(11) $[Ti(C_5H_5)_2(CO)(PhC{\equiv}CPh)]$	142	1.285(10)	1.30	1.31	*m*
(12) $[TaCl_4(PhC{\equiv}CPh)(NC_5H_5)]^-$	140(1)	1.325(12)	1.30	1.32	*l*
(13) $[Pt(PhC{\equiv}CPh)(PPh_3)_2]$	140	1.32(9)	1.30	1.32	*n*
(14) $[Pt(F_3CC{\equiv}CCF_3)(PPh_3)_2]$	140	1.255(9)	1.30	1.32	*h*
(15) $[W(CO)(PhC{\equiv}CPh)]$	140	1.30	1.30	1.32	*o*
(16) $[Ir(CO)\{C(CN){=}CHCN\}(NCC{\equiv}CCN)(PPh_3)_2]$	140	1.29(2)	1.30	1.32	*p*
(17) $[Pt\{cyclo\text{-}(CH_2)_5C{\equiv}C\}(PPh_3)_2]$	139	1.294(17)	1.30	1.32	*q*
(18) $[Nb(C_5H_5)(CO)(PhC{\equiv}CPh)_2]$	138(1)	1.35(2)	1.31	1.32	*r*
(19) $[W(S_2CNEt_2)_2(CO)(HC{\equiv}CH)]$	133(6)	1.29(1)	1.31	1.33	*s*
(20) $[W(CO)(PhC{\equiv}CPh)_3]$	130	1.30	1.31	1.33	*o*

[a] Tetrahedral orbitals at carbon: $\beta = (\theta - 125.3)°$; $r_2 = 1.316$ Å, see ref. 4. [b] Ethylene-like orbitals at carbon: $\beta = (\theta - 121.9)°$; $r_2 = 1.337$ Å, see ref. 4. [c] B. W. Davies and N. C. Payne, *Can. J. Chem.*, 1973, **51**, 3477. [d] G. R. Davies, W. Hewertson, R. H. B. Mais, P. G. Owston, and C. G. Patel, *J. Chem. Soc. A*, 1970, 1873. [e] M. Green, D. M. Grove, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1976, 759. [f] R. S. Dickson and J. A. Ibers, *J. Organomet. Chem.*, 1972, **36**, 191. [g] htpb = Hydrotris(1-pyrazolyl)borate. [h] B. W. Davies and N. C. Payne, *Inorg. Chem.*, 1974, **13**, 1843; 1848. [i] N. G. Bokiy, Yu. V. Gatilov, Yu. T. Struchkov, and N. A. Ustynyuk, *J. Organomet. Chem.*, 1973, **54**, 213. [j] B. W. Davies, R. J. Puddephatt, and N. C. Payne, *Can. J. Chem.*, 1972, **50**, 2276. [k] K. Nicholas, L. S. Bray, R. E. Davies, and R. Petit, *Chem. Commun.*, 1971, 608. [l] A. N. Nesmeyanov, A. I. Gusev, A. A. Pasynskii, K. N. Asimov, N. E. Kolobova, and Yu. T. Struchkov, *Chem. Commun.*, 1969, 739. [m] G. Fachinetti, C. Floriani, F. Marchetti, and M. Mellini, *J. Chem. Soc., Dalton Trans.*, 1978, 1398. [n] G. O. Glanville, J. M. Stewart, and S. O. Grim, *J. Organomet. Chem.*, 1967, **7**, 9. [o] R. M. Laine, R. E. Moiriarty, and R. Bau, *J. Am. Chem. Soc.*, 1972, **94**, 1402. [p] R. M. Kirchner and J. A. Ibers, *J. Am. Chem. Soc.*, 1973, **95**, 1095. [q] M. A. Bennett, G. B. Robertson, P. O. Whimp, and T. Yoshida, *J. Am. Chem. Soc.*, 1971, **93**, 3797. [r] A. N. Nesmeyanov, A. I. Gusev, A. A. Pasynskii, K. N. Asimov, N. E. Kolobova, and Yu. T. Struchkov, *Chem. Commun.*, 1969, 277. [s] L. Ricard, R. Weiss, W. E. Newton, G. Chen, and J. W. McDonald, *J. Am. Chem. Soc.*, 1978, **100**, 1318.

of two pairs of values for r_2 and β is assumed: (*a*) those calculated theoretically from tetrahedrally hybridised orbitals, $r_2 = 1.316$ Å and $\beta = 125.3°$; or (*b*) those observed in ethylene, $r_2 = 1.337$ Å and $\beta = 121.9°$.

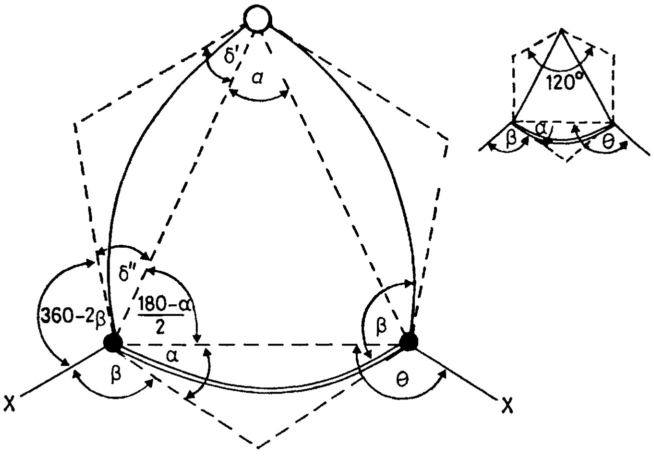

FIGURE 2 Geometry of bent-bond metallocene model for the $[TaCl_4(PhC{\equiv}CPh)(NC_5H_5)]^-$ anion, assuming ethylene-like orbitals at carbon [$a = 37.4$, $\theta = 139.9$, $\beta = 121.9$, $\alpha = (139.9 - 121.9) = 18.0$, $\delta' = (120 - a)/2 = 41.3$, $\delta'' = (121.9 - 71.3 - 18.0) = 32.6°$]

The results of the comparison are shown in Table 1 and show reasonably good agreement; where the agreement is relatively poor it can be argued that neither of the assumed r_2 values is appropriate. For Cotton's tantalum complex the agreement is good, indicating that his bonding model (II) is more appropriate than (III).

Metal–carbon bond lengths can be calculated similarly: if r_1 is the M–C single-bond length and the angle between the M–C arc and interatomic axis is δ, the apparent linear M–C distance is given by (2). It is necessary to assume

$$r/r_1 = (360/2\pi)(\sin\delta)/\delta \qquad (2)$$

that δ is the mean of two values: δ' for the angle next to the metal atom [in Cotton's tantalum complex 2δ is given by the interorbital angle (assumed 120°) minus the observed CMC angle (*a*)] and δ'' for the angle next to carbon, calculated from the angles α, β, and *a*. The value used for r_1, 2.22(2) Å, was derived from the Ta–Cl bond length of 2.44(2) Å in the same complex and is consistent with the covalent radii 1.45(2) for Ta, 0.99 for Cl, and 0.77 Å for C. This may be compared with, for example, values of 2.18(1) and 2.25 Å for the Ta–CH_3 distances in the complexes $[TaMe_2(C_5Me_5)(C_6H_4)]$ and $[Ta(CH_2)Me(C_5H_5)_2]$, respectively.[6,7]

Assuming that the Ta–C bond has a length of 2.22(2) Å and is bent as indicated, the Ta–C distance in the complex is calculated to be 2.07(2) Å. This is very close to the observed Ta–C distances in the crystal, 2.066(8) and 2.079(8) Å (mean 2.072 Å).[1] Apparently, the bent-bond metallocene model, (II), fits well in this particular case and four-electron donation from the acetylene to the metal, as in (III), need not be invoked.

Metal–Carbon Distances in Other Complexes.—The results of calculations similar to that above are summarized in Table 2. With few exceptions, the agreement with observed values is good.

TABLE 2

Calculated and observed metal–carbon distances (Å) in some acetylene complexes

Complex	M–C* Single bond	Observed	Calculated
(1)	2.11	2.278(5)	2.03
(3)	2.11	2.025(5)	2.03
(4)	2.11	2.01(3)	2.03
(6)	2.11	2.018(6)	2.01
(8)	2.11	2.07(4)	2.00
(9)	2.18	2.048	2.06
(10)	2.42	2.25	2.27
(11)	2.27	2.17	2.17
(12)	2.22	2.07	2.07
(14)	2.18	2.027(4)	2.04
(18)	2.43	2.19	2.26

* Distances are M–C(methyl) in these or from related compounds.

The only case in which the observed metal–carbon distance is significantly longer than predicted is that in complex (1). This has been attributed to the *trans* influence of the methyl ligand.

I am currently exploring the application of this approach, using simple bent-bond models, to other acetylene and olefin complexes.

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