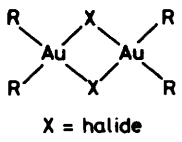
Cyano- and Halogeno-bridged Transition-metal Complexes. Structural Comparisons of Neutral and Cationic Oligomers †

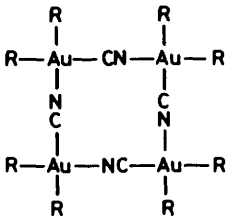
Julian A. Davies *
Department of Chemistry, College of Arts and Sciences, University of Toledo, Toledo, Ohio 43606, U.S.A.
Joel F. Liebman *
Department of Chemistry, University of Maryland Baltimore County, Catonsville, Maryland 21228, U.S.A.

The structures of some neutral and cationic oligomeric transition-metal complexes with bridging Cl and CN groups are discussed. Application of the method of structural fragments leads to the expectation of bent M–Cl–M and linear M–CN–M bridges in oligomeric complexes, resulting in the formation of dimeric chloride-bridged complexes and tetrameric cyanide-bridged complexes. These structures are found for neutral oligomers, but for charged species an additional electrostatic repulsion term is shown to be an important factor in determining the degree of oligomerization.

Halide and cyanide complexes of the transition metals are among the most commonly encountered species in traditional co-ordination chemistry.[1,2] In particular, chloride and cyanide ligands are frequently encountered in analogous compounds, a corollary of the similar size (r_{Cl} = 1.81, r_{CN} = 1.82 Å) [3] and electronegativity (X_{Cl} = 3.2, X_{CN} = 3.3) [4] of the two anions. While numerous complexes are formed by these ligands with analogous empirical formulae, in general the degree of oligomerization of polynuclear species differs. For example, the empirical formulae of the gold(III) alkyls, $[\{Au(\mu\text{-}X)R_2\}_n]$ (X = halide or cyanide; R = alkyl) are analogous, but the halogeno-complex [5] is dimeric, (1), while the cyano-complex [6] is tetrameric, (2).



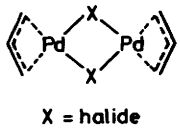
(1)



(2)

Both gold(III) and palladium(II) are d^8 systems and so it is not surprising that an identical situation occurs with the isoelectronic palladium(II) η^3-allyl complexes $[\{Pd(\mu\text{-}X)(\eta^3\text{-allyl})\}_n]$ where the chloro-complex, (3), is dimeric [7] whilst the cyano-complex, (4), is tetrameric.[8] *X*-Ray crystallographic data are available for (1),[5] (2),[6] and (3),[7] whilst (4) [8] has been shown to be tetrameric by unambiguous chemical evidence.

The difference in the degree of oligomerization is, of course, related to the tendencies of the chloride and cyanide ligands to form, respectively, bent and linear bridges between metal centres. This difference in behaviour between two otherwise similar ligands is entirely as expected. Indeed, the difference in geometry of these two bridging units does not arise from any electronic differences between Cl^- and CN^- (ref. 9) or indeed from any interaction with the metal *d* orbitals and this may be clearly seen by a consideration of the bent and linear geometries of the related species H_2Cl^+ (ref. 10) and $HCNH^+$



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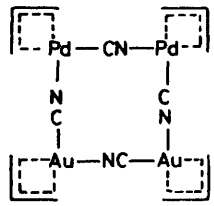


(4)

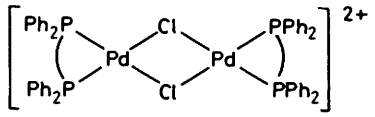
(ref. 11), and of the similarly related isoelectronic neutral pair H_2S and HCCH.[12]

There are many predictive approaches to molecular structure which can be utilized to explain the differences in behaviour between bridging chloro- and cyano-groups. In particular, the method of structural fragments [13] shows that the origin of the seeming disparity of the bridging Cl and CN cases may be ascribed to the comparative ease of donating, sharing, or ionizing a σ or π electron. While both HCl and HCN have ground state $^2\pi$ molecular ions, corresponding to the loss of a π electron, the $^2\Sigma - {}^2\pi$ energy difference in HCN is only 9 kcal mol^{-1}, compared to 81 kcal mol^{-1} for HCl.[14] It is expected that this same trend will be apparent for arbitrary RCl and RCN species and, if this is indeed the case, then any R_2Cl^+ and R–Cl–R species, including the transition-metal complexes described above, will be bent and the apparently analogous $RCNR^+$ and R–CN–R species will instead be linear.

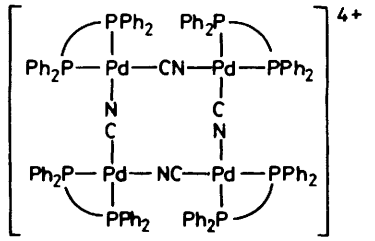
This approach thus leads to the generalization that analogous $[\{M(\mu\text{-}Cl)L_m\}_n]$ and $[\{M(\mu\text{-}CN)L_m\}_n]$ (L = ligand) complexes will have, respectively, bent and linear bridging units. On this basis, it would seem reasonable to predict that the chloro-[15] and cyano-bridged [16] complexes, $[\{Pd(\mu\text{-}X)(Ph_2PCH_2CH_2PPh_2)\}_n]^{n+}$ (X = Cl or CN), and other related oligomeric pairs, would have bent and linear bridges respectively and hence the dimeric and tetrameric structures of types (5) and (6).

Spectroscopic and other physical data have confirmed that the chloro-complex is indeed dimeric,[15] as expected. However, a combination of i.r., electronic, $^{13}C\text{-}\{^1H\}$ n.m.r., $^{31}P\text{-}\{^1H\}$ n.m.r., and mass spectroscopic measurements, in conjunction with conductiometric studies, were unable to ascertain the molecularity of the $[\{Pd(\mu\text{-}CN)(Ph_2PCH_2CH_2PPh_2)\}_n]^{n+}$ oligomer without ambiguity.[16] *X*-Ray crystallographic data,[17] however, show that the cyano-complex does not have the

† *Non-S.I. units employed:* cal = 4.184 J; dyn = 10^{-5} N.

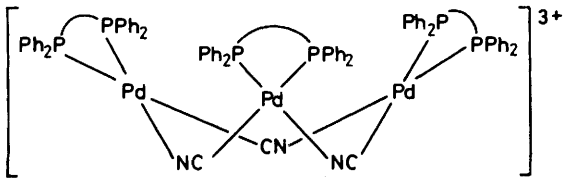


(5)



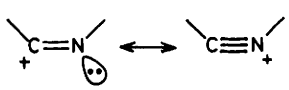
(6)

'expected' tetrameric structure but is actually a trimer, $[\{Pd(\mu\text{-}CN)(PPh_2CH_2CH_2PPh_2)\}_3]^{3+}$ (7).



(7)

The formation of a trimer in this instance causes substantial deviations from linearity in the M–CN–M bridges, resulting in a *cis*-like geometry about the CN double bond. Clearly, the energetics of distorting a linear cyano-group into a *cis*-like geometry will be more favoured than those of a *trans*-like geometry, since orbital overlap in the latter case is restricted. In the limiting case of 120° bond angles (angles MCN and MNC) this would formally correspond to overlap of a doubly occupied sp^2 orbital of nitrogen with a vacant sp^2 orbital of the positively charged carbon, as illustrated by comparison of the pairs of resonance structures (8) and (9).



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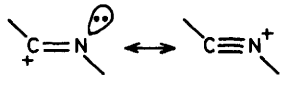
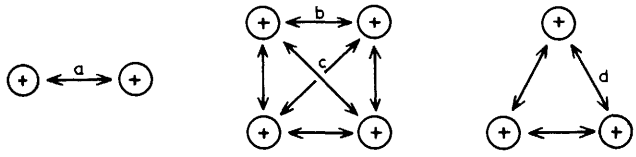


(9)

The question arises, however, as to the nature of the driving force for the formation of a trimer in preference to the 'expected' tetramer. Evidently, this is not a phenomenon peculiar to palladium(II) cyano-complexes, since the complex $[\{Pd(\mu\text{-}CN)(\eta^3\text{-allyl})\}_4]$ is indeed tetrameric. We believe that the unusual structure may be rationalized by considering the effects of the build-up of charge density on the oligomeric cations as the molecularity increases. By representing each oligomer as an array of point charges located at the metal centres, the structures (5), (6), and (7) may be considered in terms of the three charge arrays (5'), (6'), and (7').

The interionic distances, a—d, are estimated to be *ca.* 3.47, 5.24, 7.41, and 5.22 Å respectively, from representative crystallographic data.[5-7,17] To obtain an estimate of the electrostatic repulsion for each array, Coulomb's law may be applied, as the simplest approximation. In order to account for the presence of the bridging CN groups located between



(5') (6') (7')

the metal centres, we will assume a polarizable medium with a dielectric constant of 2.[18] For the geometries given in (5'), (6'), and (7') the electrostatic repulsion energies are estimated to be 48, 173, and 95 kcal mol^{-1} respectively. This factor alone would appear to favour the dimeric structure (5') but of course it is also necessary to consider the energy required to distort the bridging cyano-groups from linearity. By assuming that the co-ordination geometry of the metal centres is not distorted (*i.e.* perfect square-planar co-ordination) and that the angles M–C≡N and C≡N–M are equal, then these angles (θ) are 135, 180, and 165° for (5'), (6'), and (7') respectively. We know of no experimental data on the energetics of bending these groups from the unstrained geometry (θ = 180°) and accordingly will mimic these bends by those of acetylenes, since carbon and hydrogen are of comparable electronegativity to palladium.[4] Furthermore, qualitative reasoning suggests that although bending C≡N–Pd will be energetically more favourable than bending C≡C–X (X = C or H), the converse is equally true for bending Pd–C≡N. Within the harmonic oscillator approximation, $E = \frac{1}{2}k_\theta(\theta - 180°)^2$ where the force constants $k_\theta(C{\equiv}C) = 0.45$ mdyn $Å^{-1}$ and $k_\theta(C{\equiv}C\text{–}H) = 0.36$ mdyn $Å^{-1}$,[19] and thus the strain energies for (5'), (6'), and (7') are estimated to be 72, 0, and 12 kcal mol^{-1} respectively. It should be noted that any anharmonicity correction will have a significantly greater effect on the strain energy term for the dimer than for the trimer.

Accordingly, with these data in hand it is possible to compare the structures of both neutral and cationic cyanide-bridged oligomers. For the neutral molecules, only the strain energy term need be considered and this indicates that the tetrameric structure, (6'), is most favoured. For the ionic complexes, the electrostatic and strain energy terms may be combined to give total destabilization energies of 120, 173, and 107 kcal mol^{-1} for (5'), (6'), and (7') respectively, corresponding to values of 60, 43, and 36 kcal per mol of Pd atoms. The trimeric structure, (7'), is thus the energetically favoured oligomer when the build-up of charge density on the ionic complexes is taken into account. Furthermore, in any hypothetical equilibrium of the type: 4(trimer) ⇌ 3(tetramer), the trimer is entropically favoured.

In the case of chloride-bridged oligomers, the bent M–Cl–M unit represents a minimum of strain energy and the dimeric charge array, (5'), represents a minimum of electrostatic repulsion energy. Accordingly, these two terms are minimized for a dimeric structure in both neutral and ionic cases.

In conclusion, the well known dimeric structures of simple transition-metal chloride-bridged oligomers are favoured by both the electrostatic and strain energy terms and hence are found for both neutral and ionic complexes. In contradistinction, the tetrameric structures of cyano-bridged oligomers are favoured only by the strain energy term and hence are found for neutral complexes whereas the over-riding effects of electrostatic repulsion lead to trimeric structures for charged complexes.

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