carbon stretching frequencies[9,10] (allyl halides, 1640–1650 cm^{-1}; diallylzinc, 1610 cm^{-1}; diallylmagnesium, 1575 cm^{-1}).

Various allyl compounds of the main group elements Mg, Zn, and Cd have been investigated by nmr over a broad range of temperatures. With one exception, all the recorded allyl spectra have AB$_4$ character at every temperature studied.[11] It is conceivable, but not yet proven, that the magnetic equivalence of the C-1 and C-3 protons in these allyl systems occurs *via* intermolecular exchange of allyl groups; the greater the compound ionic character the larger the exchange rate.[15] Since the electropositive nature of the metal in main group allyl compounds would be expected to increase in the order Cd < Zn < Mg < Li,[16] one might anticipate that allyllithium in THF would likewise give an AB$_4$ allyl spectrum over the full temperature range -90 to $+40°$. Nevertheless, in practice this proves not to be the case. A possible explanation for the AB$_4$ → AA′BB′C allyl transition observed in the nmr of both THF and diethyl ether solutions of allyllithium is afforded by results of differential vapor-pressure measurements[17] on these systems.

From colligative property studies that we have carried out on allyllithium in donor solvents at 25° it can be inferred that allyllithium is aggregated in both THF and diethyl ether at concentrations similar to those employed in the nmr investigations. At a formal allyllithium concentration of 1.5 *M* in diethyl ether the apparent degree of allyllithium aggregation is $n_{\text{app}} > 10$. With 0.8 *M* allyllithium in THF, the maximum concentration amenable to colligative property measurements, $n_{\text{app}} > 1.4$. It is suggested, therefore, that the apparent substantial increase in lifetime of the allyllithium species $[\text{AA'BB'C}]^{\delta-}\text{Li}^{\delta+}$ in these solvents with decrease in temperature might be related to its propensity to self-associate.

An extended comparison is being made between allyllithium and the allyl compounds $(\text{C}_3\text{H}_5)_2\text{M}$, M = Mg. Zn Cd, and Hg. The relationship between proton chemical shifts and ionic character and the effect of strong bases (*e.g.*, N,N,N′,N′-tetramethylethylenediamine, sparteine, and hexamethylphosphoramide) are under investigation.

(9) G. Wilke, B. Bogdanovič, P. Hardt, P. Heimbach, W. Keim, M. Kröner, W. Oberkirch, K. Tanaka, E. Steinrücke, D. Walter, and H. Zimmerman, *Angew. Chem. Intern. Ed. Engl.*, **5**, 151 (1966).

(10) C. Prévost, M. Gaudemar, L. Miginiac, F. Bardone-Gaudemar, and M. Andrač, *Bull. Soc. Chim. France*, 679 (1959).

(11) AB$_4$ allyl spectra are observed with allylmagnesium bromide–diethyl ether[5] between -80 and $+33°$, diallylmagnesium–tetrahydrofuran (THF)[9,12] between -60 and $+37°$, and diallylcadmium–THF[13] between -100 and $-20°$, above which temperature it decomposes. Only with diallylzinc–THF[9,14] has a pronounced change been observed with variation in temperature; an AB$_4$ allyl → ABCD$_2$ σ-allyl transition is reported[9] to occur at $-100°$.

(12) P. West, unpublished data.

(13) K.-H. Thiele and J. Kohler, *J. Organometal Chem.* (Amsterdam), 7, 365 (1967).

(14) K.-H. Thiele and P. Zdunneck, *ibid.*, **4**, 10 (1965).

(15) Consistent with this idea is the broad ABCD$_2$ σ-allyl proton nmr spectrum observed for neat diallylmercury at 37°, which sharpens up dramatically on dilution with solvent and/or lowering the temperature.[12]

(16) (a) W. Strohmeier, *Z. Elektrochem.*, **60**, 58 (1956); (b) J. A. Ladd, *Spectrochim. Acta*, **22**, 1157 (1966); (c) M. Witanowski and J. D. Roberts, *J. Am. Chem. Soc.*, **88**, 737 (1966), and references therein.

(17) P. West and R. Waack, *ibid.*, **89**, 4395 (1967).

Peter West, John I. Purmort, Suzanne V. McKinley
The Dow Chemical Company, Eastern Research Laboratory
Wayland, Massachusetts 01778

Received October 23, 1967

The Crystal and Molecular Structure of a Tetracyanoethylene Complex of Platinum[1]

Sir:

The study of hydrocarbon complexes of transitional metals has contributed greatly to the advancement of coordination chemistry. More recently, investigations of fluorocarbon[2] derivatives of metals have provided deeper insight into the nature of the transitional metal–carbon bond. When H atoms in hydrocarbons are replaced by F atoms, a wider variety of more stable complexes may be prepared, and in many instances the nature of the bonding in the fluorocarbon complexes is significantly different from that in analogous hydrocarbon complexes.[3] A new class of metal–carbon bonded complexes has recently been reported[1c,d] where an olefinic cyanocarbon, tetracyanoethylene (TCNE), is covalently bonded to a transitional metal. These cyanocarbon complexes are noteworthy for being extremely stable relative to the hydrocarbon and fluorocarbon analogs. Heretofore, little could be said about the nature of bonding in these complexes because structural data were not available.

We report herein preliminary results of an X-ray analysis of the first example of a transitional metal–tetracyanoethylene complex, $\text{Pt(Ph}_3\text{P)}_2\text{TCNE}$. The molecular structure is unique in regard to the structural characteristics of the coordinated tetracyanoethylene and expands the concept of metal–olefin bonding.

Colorless crystals of $\text{Pt(Ph}_3\text{P)}_2\text{TCNE}$ suitable for crystallographic examination were obtained from the reaction of *trans*-$\text{PtHCl(PPh}_3)_2$ and tetracyanoethylene in benzene at room temperature, followed by slow recrystallization over a several day period from benzene–ethanol. The compound crystallizes in the monoclinic system with unit cell parameters $a = 17.506 \pm 0.009$ Å, $b = 11.234 \pm 0.008$ Å, $c = 18.521 \pm 0.013$ Å, and $\beta = 97°\ 10' \pm 10'$. The space group is $P2_1/c$ and $Z = 4$. The X-ray intensities were obtained (Cu Kα radiation) with Weissenberg film methods (*h*0*l* through *h*7*l*) and recorded with a Joice–Loebl flying-spot microdensitometer. The structure was resolved by three-dimensional Patterson–Fourier methods and refined by isotropic least-squares block diagonal techniques. At the present stage of refinement, the *R* index calculated on 2042 observed reflections is 12%. The geometry of the metal coordination is shown in Figure 1, and the most important bond lengths and angles with their estimated standard deviations are listed.

Several salient features are to be noted. The dihedral angle between the planes P_1PtP_2 and C_1PtC_2 is 10°. The TCNE moiety is distorted from planarity upon coordination such that the angle between a line through C_1–CN and the plane which passes through C_1 and C_2, and which is perpendicular to the P_1PtP_2 plane, is about 10°. The C_1–C_2 bond length is 1.52 Å, which is close to that of a carbon–carbon single bond. The mean length of the carbon–carbon bonds of the C—CN

(1) For W. H. B., this communication is part V in the series Metal Complexes of Cyanocarbons; (a) part IV, P. Uguagliati and W. H. Baddley, manuscript in preparation; (b) part III, W. H. Baddley, *J. Am. Chem. Soc.*, in press; (c) part II, *ibid.*, **88**, 4545 (1966); (d) part I, W. H. Baddley and L. M. Venanzi, *Inorg. Chem.*, **5**, 33 (1966).

(2) P. M. Treichel and F. G. A. Stone, *Advan. Organometal. Chem.*, **25**, 33 (1966).

(3) See, for example, P. B. Hitchcock and R. Mason, *Chem. Commun.*, 242 (1967).

units in the complex is 1.40 ± 0.04 Å as compared to the mean value of 1.449 Å in uncoordinated TCNE. The two independent platinum–carbon bond lengths are practically the same. Additionally, the two platinum–phosphorus bond lengths are also equal.

It is pertinent to point out that recently[4] it has been reported that $Ni(Ph_3P)_2(C_2H_4)$ exhibits a deviation from strict planarity, as has also been observed in $Pt(Ph_3P)_2$-(PhC≡CPh) and $Pt(Ph_3P)_2(CS_2)$ in which the CPtC and CPtS planes are inclined at angles of 14 and 6°, respectively, to the PPtP plane.[5,6] There appears to be no obvious electronic or steric reason for the slight deviation from planarity, and it may be, as suggested by others,[4] that a low-energy barrier to rotation of the ligand out of the PPtP plane is indicated.

The most significant structural feature of $Pt(Ph_3P)_2$-TCNE is the long "olefinic" bond distance of 1.52 Å, which is 0.21 Å longer than the C=C distance in tetracyanoethylene itself.[7] For a number of metal–olefin complexes which have been examined crystallographically, carbon–carbon bond distances lie in the range 1.40–1.47 Å, which is about 0.1 Å longer than the C=C distances of the uncomplexed olefins.

There are two ways of viewing the bonding in $Pt(Ph_3P)_2TCNE$. One can consider C_6N_4 to be a dicarbanion functioning as a bidentate ligand with two σ bonds to the platinum such that a three-membered ring is extant, *i.e.*, a "platinacyclopropane" structure. From the very small C_1PtC_2 bond angle of 42°, it might be surmised that considerable strain would exist in this system and that the compound might be unstable. However, $Pt(Ph_3P)_2TCNE$ is exceedingly stable thermally and decomposes at 268–270°.

The bonding may alternatively be interpreted in the context of the Dewar–Chatt–Duncanson model[8] of metal–olefin bonding, and, since the donor properties of the C=C bond of TCNE would seem to be almost negligible for formation of a metal–olefin σ bond, the tetracyanoethylene could be visualized as being bonded to platinum by an essentially "pure π bond." In view of the fact that TCNE is one of the strongest π acids known,[9] the electron pair in the complex which occupies a molecular orbital of π symmetry (metal d + olefin π*) may be localized mainly on the TCNE moiety, and the carbon–carbon bond order would thereby be reduced to one, which is consistent with the C_1–C_2 bond length. Also, a shortening of the C–CN distance is consistent with this model, since molecular orbital calculations have shown that the addition of electrons to the antibonding orbitals of TCNE to form $TCNE^-$ and $TCNE^{2-}$ causes an *increase* in the bond order of the C–CN bond.[10]

It is important to point out that the description of the bonding in $Pt(Ph_3P)_2TCNE$ in terms of the Dewar–Chatt–Duncanson molecular orbital model is completely equivalent to the valence bond description which depicts a three-membered σ-bonded ring framework. Thus a "pure π bond" and a "platinacyclopropane" ring for $Pt(Ph_3P)_2TCNE$ are physically the same in terms of atomic orbitals used.[11] The molecular orbital approach may be preferable because of its flexibility in treating intermediate cases where both metal → olefin π bonding and olefin → metal σ bonding are important in the over-all bonding scheme. For example, in the series of complexes, $Pt(Ph_3P)_2$(cyano-substituted ethylene), one can anticipate gradations in structural (and other) features of the coordinated olefin as the H atoms of ethylene are successively substituted by cyano groups, this gradation arising because of the varying degree to which the metal d orbitals mix with the π and/or π* orbitals of the olefin as the energies of these orbitals are progressively lowered by increased cyanide substitution on the olefinic carbon atoms. To this end, we[12] have prepared complexes of the type $Pt(Ph_3P)_2$(cyanoolefin) (cyanoolefin = acrylonitrile, fumaronitrile, and diphenylmethylenemalononitrile) in order to compare their chemical and structural features with $Pt(Ph_3P)_2TCNE$.

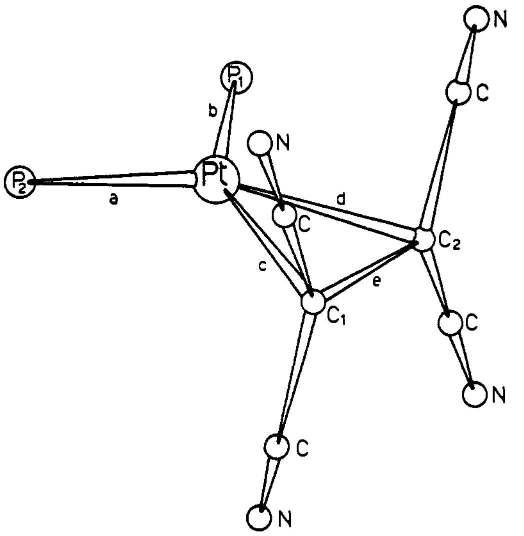

Figure 1. Configuration of $Pt(Ph_3P)_2TCNE$. Bond lengths and angles are: $a = 2.29 \pm 0.01$ Å; $b = 2.30 \pm 0.01$ Å; $c = 2.10 \pm 0.03$ Å; $d = 2.11 \pm 0.03$ Å; $e = 1.52 \pm 0.03$ Å; $\angle ab = 101 \pm 0.3°$; $\angle cd = 42 \pm 1.4°$; $\angle ac = 110 \pm 0.8°$; $\angle bd = 104 \pm 0.8°$. The bond lengths and angles in the triphenylphosphine groups are normal. The mean values in the C—C≡N groups are: C–C = 1.40 ± 0.04 Å; C–N = 1.15 ± 0.05 Å; $\angle$C–C–N = 168 ± 10°.

Acknowledgments. We wish to thank Dr. P. Uguagliati for helpful discussion. The work done at the Centro di Strutturistica Chimica, Padova, was supported by the Italian Consiglio Nazionale delle Richerche (C.N.R.). Research carried out at the Louisiana State University was supported by National Science Foundation Grant GP-6769.

---

(4) C. D. Cook, C. H. Koo, S. C. Nyburg, and M. T. Shiomi, *Chem. Commun.*, 426 (1967).

(5) J. O. Glanville, J. M. Stewart, and S. O. Grim, *J. Organometal. Chem.* (Amsterdam), 7, P9 (1967).

(6) M. Baird, G. Hartwell, R. Mason, A. I. M. Rae, and G. Wilkinson, *Chem. Commun.*, 92 (1967).

(7) D. A. Bekoe and K. N. Trueblood, *Z. Krist.*, **113**, 1 (1960).

(8) M. J. S. Dewar, *Bull. Soc. Chim. France*, **18**, C79 (1951); J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

(9) R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).

(10) B. R Penfold and W. N. Lipscomb, *Acta Cryst.*, **14**, 589 (1961).

(11) This situation is not unlike the alternative ways that may be used to describe the bonding in ethylene. In a molecular orbital description, a σ and a π bond are visualized, but these are the same mathematically as two equivalent bent bonds in a valence bond approach; see J. A. Pople, *Quart. Rev.* (London), **11**, 273 (1957).

(12) W. H. Baddley and J. M. Singer, to be published.

C. Panattoni, G. Bombieri, U. Belluco
Instituto di Chimica Generale
University di Padova, Padua, Italy

W. H. Baddley
Coates Chemical Laboratory, The Louisiana State University
Baton Rouge, Louisiana 70803

Received November 13, 1967