energies of the anions.[9] Indeed, a satisfactory correlation exists between corresponding $\Delta F°(R^-)$ and $\delta\Delta$ values with slope of 1.3 kcal/ppm.

Table I. Stabilization Energies of Substituted Trityl Anions in Dimethyl Sulfoxide

Substituent	$E°(2)$, v	$\Delta F°(R^-)$ kcal/mole (±0.2)	$\bar{\sigma}^-$	$\delta\Delta$, ppm
H	(0.000)	(0.0)	0.00	(0.0)
p-F	0.020[a]	−0.5	−0.03[c]	0.0
p-CH_3	0.056	−1.4	−0.17	1.6
p-CH_3O	0.209[b]	−4.8	−0.47[c]	3.3
p-$(CH_3)_2N$	0.218	−5.0	−0.52[c]	3.8
p-NO_2	−0.685	15.8	+1.63[c]	−12.1
Tris-*p*-NO_2	−0.697	18.5	+0.67[d]	....
m-NO_2	−0.291[b]	6.7	+.71	....
m-CF_3	−0.175	4.0	+.48	....

[a] Approximate value. [b] Polarographic reduction of the corresponding hexaarylethanes gave $\Delta E_{1/2}$ values agreeing within experimental error with $E°(2)$ values. [c] Calculated by the procedure of Taft and Lewis, *J. Am. Chem. Soc.*, **81**, 5351 (1959). Values are the mean of those obtained from $\Delta F°(R^-)$ and $\delta\Delta$ values. [d] Value per NO_2 group.

Using the procedure of Taft and Lewis,[10] the $\Delta F°(R^-)$ values yield a ρ value for reaction 2 of −6.9 (in log K units) and the $\bar{\sigma}^-$ values listed in Table I. The magnitudes of the values of ρ and $\bar{\sigma}^-$ for *p*-NO_2 are noteworthy in that both exceed corresponding values previously reported for carbanion[11] or similar reactivities,[10] in accord with expectations for reaction 2. For *p*-F and *p*-OCH_3, $\bar{\sigma}^-$ values are more negative than normal,[12] a result in accord with Mulliken's concept of concerted inductive–mesomeric action.[10–13] The results of Table I and similar reactivities[10] in fact indicate that *the π donor destabilizing effects of p-F, p-OCH_3, p-$N(CH_3)_2$* (and probably all other UAFPD substituents[14]) *become essentially identical when substituted at electron-rich unsaturated carbon* ($\sigma^-_R = -0.60 \pm 0.06$).[15] This striking result (which may be seen in terms of σ_R not σ values) can be readily accommodated by the Mulliken concept and in fact provides convincing evidence thereof.

Polar effects (field and inductive) on reactivities are known to be approximately additive.[16] We wish to emphasize in contrast the marked "saturation" of conjugative π electronic *stabilization* effects which are dramatically illustrated in Table I and by other recent results.[3,9,17] The ratio (1.17) of the stabilization energies of tris-*p*-NO_2- to mono-*p*-NO_2-trityl anions is markedly less[18] than the additive factor of 3. Similarly for trityl cations, the ratio of the stabilization energies of tris-*p*-$N(CH_3)_2$ to mono-*p*-$N(CH_3)_2$ is 1.61.[3] No additional stabilization energy has been found for the $(CH_3O)_3C^+$ cation compared to that for the $(CH_3O)_2CH^+$ cation, both relative to CH_3^+.[17] A general trend toward *increased "saturation" of multiple substitutional π electronic stabilization effects with increased magnitude of the π stabilization effect is clearly evident.*[2,3,17]

These multiple substitution effect results provide a clear negative answer to the question of whether a set of conjugation-enhanced substituent parameters (*e.g.*, σ^+, σ^-, or $\Delta\sigma_R^{\pm}$) may be formulated which have wide general applicability.[10,19–21] Compare, for example, the markedly different effective (formal) $\bar{\sigma}^-$ values for mono-*p*-NO_2- and for tris-*p*-NO_2-trityl anions (Table I). While it must be recognized that *para*-substituent effects in trityl cations and anions are subject to steric effects of phenyl twisting at the central carbon,[22] we believe the results in these systems are of such magnitudes as to indicate that the above generalization also holds for "intrinsic" π electronic behavior in coplanar systems. This conclusion is supported by the results of model HMO calculations of the electron affinities and ionization potentials of *para*-substituted trityl radicals (relative to trityl) for both twisted and hypothetical coplanar ions.[2]

It is finally of interest to note that $\Delta F°(R^-) - \Delta F°(R^+)$ corresponds to the standard free energy change for reaction 4, which gives the substituent

$$R^- + R_0^+ \rightleftarrows R^+ + R_0^- \tag{4}$$

effect on the Mulliken electronegativity[23] ($\Delta I + \Delta A$) of trityl radicals. Since $\Delta F°(R^-)$ and $\Delta F°(R^+)$ values are not available in a common solvent, $\Delta I + \Delta A$ may only be approximated by the available data. The results conform to the $\sigma\rho$ features which have been discussed in connection with reactions 1 and 2.

---

[9] R. W. Taft and L. D. McKeever, *J. Am. Chem. Soc.*, **87**, 2489 (1965).

[10] R. W. Taft and I. C. Lewis, *ibid.*, **81**, 5351 (1959).

[11] A. Streitwieser, Jr., and H. F. Koch, *ibid.*, **86**, 404 (1964).

[12] R. W. Taft, *et al.*, *ibid.*, **81**, 5352 (1959).

[13] R. S. Mulliken, *Tetrahedron*, **5**, 253 (1959).

[14] R. W. Taft, *et al.*, *J. Am. Chem. Soc.*, **85**, 3146 (1963).

[15] Note further that this is slightly more negative than the σ^0_R value for $N(CH_3)_2$; the only deviations of consequence to this generalization appear for the *p*-NH_2 and *p*-$N(CH_3)_2$ substituents in the ionization of phenols (in contrast, in the ionization of anilinium ions the generalization holds). We propose the less negative σ^-_R values in this case result from hydrogen bonding of these substituents to water which is induced in the phenoxide ions.

[16] *Cf.* R. W. Taft in Ed., M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N.Y., 1956, Chapter 13.

[17] (a) R. H. Martin, F. W. Lampe, and R. W. Taft, *J. Am. Chem. Soc.*, **88**, 1353 (1966); (b) *cf.* also J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N.Y., 1962, p 101.

[18] A similar factor has been obtained by C. D. Ritchie and R. E. Uschold (private communication) in the ionization of the triarylmethanes in DMSO.

[19] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

[20] H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **79**, 1913 (1957).

[21] Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Japan*, **32**, 971 (1959).

[22] (a) R. I. Walter, *J. Am. Chem. Soc.*, **88**, 1930 (1966); (b) F. J. Adrian, *J. Chem. Phys.*, **28**, 608 (1958).

[23] R. S. Mulliken, *ibid.*, **2**, 782 (1934); **3**, 573 (1935).

L. D. McKeever, R. W. Taft
Department of Chemistry, University of California, Irvine
Irvine, California

Received August 22, 1966

Tetracyanoethylene Complexes of Rhodium and Iridium[1]

Sir:

The fact that the nature of the transition metal–carbon σ bond is not well understood has been noted in reviews.[2] A cursory survey of the literature in-

---

[1] Paper II of the series: Metal Complexes of Cyanocarbons. Part I: W. H. Baddley and L. M. Venanzi, *Inorg. Chem.*, **5**, 33 (1966).

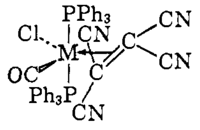
[2] (a) G. E. Coates and F. Glockling, "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, Chapter 9; (b) P. M. Trieichel and F. G. A. Stone, *Advan. Organometal Chem.*, **1**, 177 (1964).

dicates that a decrease in "softness"[3] of the carbon atom of the M–C σ bond results in more stable complexes. For example, by replacing H atoms by F atoms in alkanes and alkenes, various workers have been able to prepare a large number of fluorocarbon complexes of transition metals,[2b] and in many cases the analogous hydrocarbon complexes have not been prepared or are very unstable. We are exploring in this laboratory the general area of metal–carbon σ-bonded complexes by using cyanocarbons as ligands, the strategy being that cyano groups may be particularly effective in stabilizing the metal–carbon bond because such a group attached to a carbon atom may "harden" it more than a fluorine or hydrogen substituent, since the latter are not capable of withdrawing electron density *via* a π-acceptor route as is the $C\equiv N$ group.

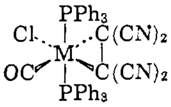
Reported herein is the preparation of the first examples of a well-known cyanocarbon, tetracyanoethylene (TCNE), covalently bonded to rhodium and iridium. The stabilities of these new compounds are quite noteworthy relative to analogous hydrocarbon and fluorocarbon complexes, and these crystalline substances are particularly relevant as possible models for intermediates which have been proposed in the homogeneous catalytic hydrogenation of olefins by rhodium and iridium substrates.

Reaction of the d^8 square-planar carbonyl complexes[4,5] of the type $[M(Ph_3P)_2CO(X)]$ (M = Rh, X = Cl, Br, NCS; M = Ir, X = Cl) suspended or dissolved in benzene with equilmolar amounts of tetracyanoethylene dissolved in benzene at room temperature (30°) gives complexes of the type $M(Ph_3P)_2CO(X)$-TCNE. With M = Rh and X = Cl, for example, golden powdery crystals are obtained after recrystallization from benzene–hexane. *Anal.* Calcd for $RhC_{43}H_{30}OP_2N_4Cl$: C, 63.05; H, 3.69; N, 6.90; Cl, 4.33; mol wt, 819. Found: C, 63.26; H, 3.99; N, 6.73; Cl, 4.50; mol wt, 645.[6] The infrared spectrum in CH_2Cl_2 solution includes bands at 2075 (very strong, sharp) and 2230 cm^{-1} (medium), which are the $C\equiv O$ and $C\equiv N$ stretching fequencies, respectively. The analogous iridium complex is obtained as very pale yellow crystals after recrystallization from $CHCl_3$–EtOH. *Anal.* Calcd for $IrC_{43}H_{30}OP_2N_4Cl$: C, 56.85; H, 3.3; Cl, 3.91; P, 6.82; N, 6.17. Found: C, 56.85; H, 3.27; Cl, 4.20; P, 6.93; N, 6.30. The infrared spectrum in CH_2Cl_2 includes bands at 2060 (very strong, sharp) and 2235 cm^{-1} (medium). The thiocarbonyl complexes[7] $[Rh(Ph_3P)_2CS(X)]$ (X = Cl, Br) react with tetracyanoethylene in an equally facile manner to give the products $Rh(Ph_3P)_2CS(X)$-TCNE. For X = Cl, golden crystals were obtained after recrystallization from CH_2Cl_2–hexane. *Anal.* Calcd for $RhC_{43}H_{30}P_2S_1N_4Cl$: C, 61.84; H, 3.62; P, 7.41; S, 3.83; N, 6.70; Cl, 4.24. Found: C, 61.79; H, 3.99; P, 7.60; S, 3.70; N, 6.74; Cl, 4.37. The complex $Rh(Ph_3P)_2CS(Cl)TCNE$ in CH_2Cl_2 solution exhibits infrared bands at 1355 (very strong) and 2235 cm^{-1} (medium) which correspond to the $C\equiv S$ and $C\equiv N$ stretching frequencies, respectively. All the compounds reported herein are crystalline and appear to be stable indefinitely in the solid state. The rhodium complexes tend to decompose in solution over a period of time. The iridium complex is rather more stable in solution, and may, for example, be recovered from boiling $CHCl_3$ or boiling benzene.

These complexes may be formulated as either five-coordinate complexes of M(I) or as six-coordinate complexes of M(III)[8] as shown. The fact that the



1



2

$C\equiv O$ stretching frequencies in these TCNE adducts are *ca.* 100 cm^{-1} higher than the $C\equiv O$ stretching frequencies of the square-planar M(I) precursors indicates that the central metal ion has acquired a more positive charge on coordinating with the cyanoolefin. These $C\equiv O$ stretching frequencies fall in the same range as those previously observed for *bona fide* M(III) compounds. For a series of complexes of the type $[Ir(R_3L)CO(X)_3]$ (X = Cl, Br; L = P, As, Sb; R = alkyl, aryl), the $C\equiv O$ stretches for 13 compounds were in the 2000–2100-cm^{-1} range.[9] Furthermore, the TCNE adduct of the thiocarbonyl complex $Rh(Ph_3P)_2CS(Cl)$ has the $C\equiv S$ stretching frequency at 1355 cm^{-1} compared to 1299 cm^{-1} in the Rh(I) thiocarbonyl complex.[7] For comparison, the Rh(III) complex, $Rh(Ph_3P)_2CS(Cl)_3$, has ν_{CS} at 1362 cm^{-1}. Thus it is tentatively considered that the coordinated tetracyanoethylene in these new complexes is *anionoid* in character, and that these are better described as

---

(3) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 353 (1963).

(4) L. M. Vallarino, *J. Chem. Soc.*, 2287 (1957).

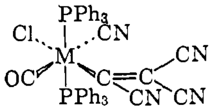
(5) L. Vaska and J. W. Diluzio, *J. Am. Chem. Soc.*, **83**, 2784 (1961).

(6) This molecular weight measurement was carried out with *ca.* 0.01 *M* solutions of the complex in $CHCl_3$ using a Mechrolab osmometer. The low value obtained is indicative of partial dissociation of the complex in solution under these conditions.

(7) M. C. Baird and G. Wilkinson, *Chem. Commun.*, 267 (1966).

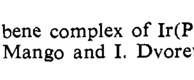
(8) Bonding of the TCNE to the metal through a nitrogen atom is ruled out because the $C\equiv N$ stretching frequencies in the complexes (*ca.* 2230 cm^{-1}) are about the same, or slightly less, than those in TCNE itself (2228 and 2260 cm^{-1}). In nitrile complexes an increase in the $C\equiv N$ stretching frequency is usually observed for the complexes relative to the uncoordinated nitrile; see, for example, B. L. Ross, J. G. Grasselli, W. M. Ritchey, and H. D. Kaez, *Inorg. Chem.*, 2, 1023 (1963).

Several plausible structures may be written for these complexes that are consistent with the analytical data. For example, a σ-tricyanovinyl complex, $M(PPh_3)_2CO(X)[C(CN)=C(CN)_2](CN)$, would be a plausible



product since it is well known that a cyano group can be displaced from TCNE by a variety of reagents: T. L. Cairns, *et al.*, *J. Am. Chem. Soc.*, **80**, 2775 (1958). Infrared data do not substantiate such a product for these particular reactions. No absorption bands are observed between 1500 and 1800 cm^{-1}, in which region the $C=C$ stretching frequency of a tricyanovinyl group might be expected.

An unlikely, but possible, product which is not strictly ruled out by any of the data would be a bis(dicyanocarbene) structure, *i.e.*



Evidence for a monocarbene complex of $Ir(Ph_3P)_2CO(Cl)$ has recently been presented: F. D. Mango and I. Dvoretzky, *J. Am. Chem. Soc.*, **88**, 1654 (1966).

(9) J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1625 (1964).

M(III) complexes (**2**). A somewhat analogous structure was proposed by Vaska for the oxygen complex $Ir(Ph_3P)_2CO(Cl)O_2$,[10] and more recently Parshall and Jones suggested a three-membered, σ-bonded ring structure for the tetrafluorethylene adduct $Ir(Ph_3P)_2CO(Cl)C_2F_4$.[11] In this connection, it is interesting to compare ν_{CO} for these two complexes with $Ir(Ph_3P)_2CO(Cl)$TCNE. For $Ir(Ph_3P)_2CO(Cl)Y$, ν_{CO} values are 2000,[10] 2040,[11] and 2058 cm^{-1} for Y = oxygen, tetrafluoroethylene, and tetracyanoethylene, respectively,[12] indicating that the transfer of electrons from metal to ligand Y increases in the order given. The O–O distance in the oxygen complex has been shown to be intermediate between that in molecular oxygen and peroxide.[13] This fact, considered in conjunction with the rather higher ν_{CO} of the TCNE complex relative to the oxygen complex, probably means that an essentially σ-bonded, three-membered "metallocyclopropane" ring structure exists in these compounds.

The stability of these rhodium and iridium cyanocarbon complexes appears to be greater than analogous hydrocarbon complexes, and equal to or somewhat greater than recently isolated fluorocarbon complexes. Vaska and Rhodes[14] noted that $Ir(Ph_3P)_2CO(I)$ reacted reversibly with ethylene at 26° and 700 mm in toluene, but due to rapid dissociation the complex was not isolated. In the case of $Rh(Ph_3P)_2CO(Cl)$, ethylene absorption was not observed. Tetrafluoroethylene was reported to react with $Ir(Ph_3P)_2CO(Cl)$ at 25° and 3 atm to give pale yellow $Ir(Ph_3P)_2CO(Cl)C_2F_4$. Solutions of this complex in benzene evolved tetrafluoroethylene at 25° under vacuum.[15]

In the homogeneous catalytic hydrogenation of ethylene by $Ir(Ph_3P)_2CO(Cl)$, an intermediate having a structure similar to that shown in **2** has been postulated.[13] Since the TCNE adduct, unlike the ethylene adduct, may be isolated as a stable, crystalline compound, physical and chemical studies may now be carried out on these model compounds that were not heretofore possible. Such studies, as well as attempts to prepare cyanocarbon complexes of other organometallic substrates, are being pursued.

---

[10] L. Vaska, *Science*, **140**, 809 (1963).

[11] G. W. Parshall and F. N. Jones, *J. Am. Chem. Soc.*, **87**, 5356 (1965).

[12] Values quoted are for solid state spectra.

[13] S. J. LaPlaca and J. A. Ibers, *J. Am. Chem. Soc.*, **87**, 2581 (1965).

[14] L. Vaska and R. E. Rhodes, *ibid.*, **87**, 4970 (1965).

[15] R. Cramer and G. W. Parshall, *ibid.*, **87**, 1392 (1965).

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

Received August 22, 1966

Book Reviews

Annual Survey of Organometallic Chemistry. Volume 1. Covering the Year 1964. By Dietmar Seyferth, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass., and R. Bruce King, Mellon Institute, Pittsburgh, Pa. American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York, N. Y. 1965. viii + 330 pp. 17 × 24 cm. $20.00.

This volume is the first in what is planned as a continuing annual digest of all the original literature on organometallic chemistry, defined as the chemistry of compounds containing at least one metal–carbon bond. It is divided into two parts of about equal length, the first covering the nontransition metals and metalloids, and the second the transition metals. The remarkable growth of research activity in organometallic chemistry is shown by the fact that this first volume, covering somewhat less than a year, lists nearly 1400 references. Merely assimilating the data in so many papers represents a prodigious effort on the part of the authors.

In order to cover all the ground, the authors have adopted a style which will be familiar to all who have used the British Chemical Society's *Annual Reports*. For others, it should be explained that the writing is not just terse, it is bikini-like in its brevity—the essentials are just barely covered. Many articles must be disposed of in single sentences which do no more than indicate their contents. The section on organozinc compounds is typical; twelve original papers are covered in 26 sentences of text. A book of this sort is not intended to be read cover to cover at one time. More than a few pages at a sitting definitely tends to make the head spin.

Within the limitations of the task, the authors have done an admirable job. The organization is very good. Patents are not covered, so the survey is largely restricted to fundamental science rather than technology, but within this framework the coverage is remarkably complete; the reviewer knows of no significant omissions from the original literature.

Brief critical comments are not uncommon, and, although they necessarily reflect the points of view of the authors, most seem well conceived and pertinent. The literary quality is high, particularly in the first half of the book dealing with the nontransition metals. In the latter half, the density of facts is less, which makes for somewhat easier going on the part of the reader. But in this section nearly every paragraph begins with the names of investigators, and the effect is a bit repetitious.

Interpretation of the text is greatly aided by numerous equations and clear structural drawings. A minor defect is that in the second half of the book, one must often turn the page to find the drawing referred to. This source of frustration could easily be alleviated. Boldface numerals rather than Roman numerals would also simplify things for the user, for the number of drawings rises as high as LXXIV and even XCVIII in some chapters.

For students and others not closely acquainted with the field, well-written reviews of particular subjects, longitudinal in time, are much more helpful than an annual digest. But for the specialist, "Annual Surveys of Organometallic Compounds" can be quite useful as a guide to the literature. Its value will increase with time if the succeeding volumes match the standards set in Volume I. This book is recommended to all good chemical libraries, and to those researchers in organometallic chemistry who wish to have this literature aid available at their fingertips.

Robert West
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706