Inorg. Chem. **1993**, *32*, 377-378 377

Molecular and Crystal Structure of a μ_2-[TCNE]$^{2-}$ Complex: [(Ph$_3$P)$_2$(OC)Ir]$_2$[TCNE]†

Gordon T. Yee,[1] Joseph C. Calabrese, Carlos Vazquez, and Joel S. Miller*

Science and Engineering Laboratories, Experimental Station, E328, Du Pont, Wilmington, Delaware 19880-0328

Received December 9, 1992

The reaction of tetracyanoethylene (TCNE) with metal coordination complexes leads to the formation of a plethora of complexes exhibiting a variety of bonding arrangements. Best characterized are the nonbonded structures found for metallocene-based charge- and electron-transfer complexes {e.g., [Fe^{II}Cp$_2$][TCNE][2] or [Fe^{III}Cp*$_2$]$^{\bullet+}$[TCNE]$^{\bullet-}$ [3] (Cp = cyclopentadienide; Cp* = pentamethylcyclopentadienide)}, platinum-group η^2-metallocyclopropane structures {e.g., [Pt(PPh$_3$)$_2$TCNE],[4a] [Ir(CO)Br(PPh$_3$)$_2$TCNE],[4b] and [Ir(CO)Br(AsPh$_3$)$_2$TCNE][4c]}, and recently reported linear chain structures with TCNE μ_2-bound to two metals [i.e., [MnTPP]$^+$[TCNE]$^{\bullet-}$ (TPP = *meso*-tetraphenylporphyrin)[5] and [M(hfacac)$_2$TCNE] (M = Cu, Co) (hfacac = hexafluoroacetylacetonate)].[6] In addition to understanding the bonding modes of TCNE and its anions, recent work has shown that some TCNE-based materials exhibit cooperative magnetic behavior.[3,7,8] To understand the mechanisms of spin coupling necessary for the observed ferromagnetic behavior, a detailed knowledge of the bonding of TCNE is essential.[5,9] This is preferably accomplished by a structural determination of the magnetic material under investigation, but for the disordered V[TCNE]$_x$·yCH$_2$Cl$_2$ room-temperature magnet, it must be determined by alternative methods using model compounds.[7-9] Herein we extend the examples of TCNE bonding to a metal with the structural characterization of [TCNE]$^{2-}$ μ_2-bound to two Ir^I's; it is the first example of the coordination chemistry of [TCNE]$^{2-}$.

The reaction of K[TCNE] and *trans*-[Ir(CO)Cl(PPh$_3$)$_2$] leads to the isolation of [Ir(CO)(PPh$_3$)$_2$]$_2$[TCNE]·MeCN (**1**) and [Ir(CO)(PPh$_3$)$_2$]$_2$[C$_4$(CN)$_6$] (**2**).[10] The latter complex forms via the dimerization of [TCNE]$^-$ and the Rh analog has been structurally characterized.[11] The structure reveals an essentially planar [C$_4$(CN)$_6$]$^{2-}$ μ_2-bound to two Rh^I's. We have prepared **1**, grown crystals[12] upon slow cooling to room temperature from acetonitrile, and structurally characterized it.[13] An ORTEP drawing of the [TCNE]$^{2-}$ and Ir^I coordination sphere is presented in Figure 1, and the average key bond distances and angles are presented in comparison to other related TCNE-based compounds in several oxidation states in Table I. It is the first example of [TCNE]$^{2-}$ σ-bound to a metal. The 2- charge on the anion is evident from the (NC)$_2$C–C(CN)$_2$ bond distance and dihedral angle. This C–C distance is 1.478 Å which is comparable to the separation of 1.49 Å observed for the free [TCNE]$^{2-}$ ion.[14] This is significantly longer than the 1.398 Å and 1.392 Å observed for [TCNE]$^{\bullet-}$ in [FeCp*$_2$]$^{\bullet+}$[TCNE]$^{\bullet-}$ [15] and [MnTPP]$^+$[TCNE]$^{\bullet-}$,[5] respectively, and 1.344, 1.353, and 1.349 Å observed for TCNE and [M(hfacac)$_2$TCNE] (M = Cu, Co)].[6] The nonplanar geometry is also characteristic of the oxidation state; TCNE and [TCNE]$^{\bullet-}$ are planar (D_{2h}) while [TCNE]$^{2-}$ is twisted (D_{2d}).[14] The observed dihedral angle is 67.2°, consistent with the free rotation along the center C–C bond, and is not 90° due to packing forces. This value is smaller than the 87.1° reported for the isolated free [TCNE]$^{2-}$ ion.[14]

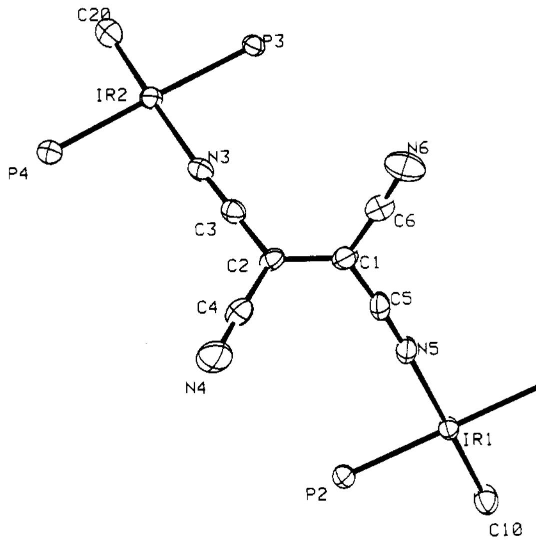


Figure 1. Structure of the P$_2$C$_2$Ir$_2$[TCNE] framework for [(Ph$_3$P)$_2$(OC)Ir]$_2$[TCNE]. The key anion distances are C(1)–C(2) = 1.478(8), C(1)–C(5) = 1.366(9), C(1)–C(6) = 1.426(9), C(2)–C(3) = 1.375(8), C(2)–C(4) = 1.407(9), N(3)–C(3) = 1.160(7), N(4)–C(4) = 1.152(8), N(5)–C(5) = 1.168(8), and N(6)– C(6) = 1.147(8) Å.

The Ir—N≡C angle is essentially linear (175.0°) and is comparable to those reported for **2** (168.8°), MnCp(CO)$_3$TCNE (181.1°),[16] and [RuP(OMe)$_3$PPh$_3$Cp(C$_3$(CN)$_5$)] (176.3°)[17a] and the values of 164.7 and 168.8° reported for [M(hfacac)$_2$TCNE] (M = Cu, Co)[6] but is not comparable to that reported for

---

† Contribution No. 6393.

[1] Current address: Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309.

[2] Adman, E.; Rosenblum, M.; Sullivan, S.; Margulis, T. N. *J. Am. Chem. Soc.* **1967**, *89*, 4540.

[3] Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* **1988**, *88*, 201.

[4] (a) Baddley, W. H.; Venanzi, L. M. *Inorg. Chem.* **1966**, *5*, 33. (b) McGinnety, J. A.; Ibers, J. A. *J. Chem. Soc., Chem. Commun.* **1968**, 235. (c) Dunn, J. P. R.; Jacobs, R.; Fritchie, C. J., Jr. *J. Chem. Soc., Dalton Trans.* **1972**, 2007.

[5] Miller, J. S.; Calabrese, J. C.; McLean, R. S.; Epstein, A. J. *Adv. Mater.* **1992**, *4*, 498.

[6] Bunn, A. G.; Carroll, P. J.; Wayland, B. B. *Inorg. Chem.* **1992**, *31*, 1297.

[7] Manriquez, J. M.; Yee, G. T.; McLean, R. S.; Epstein, A. J.; Miller, J. S. *Science* **1991**, *252*, 1415.

[8] Epstein, A. J.; Miller, J. S. In *Conjugated Polymers and Related Materials: The Interconnection of Chemical and Electronic Structure*; Salaneck, W. R., Lündstrom, I., and Rånby, B., Eds.; Proceedings of Nobel Symposium NS-81; Oxford University Press: London, 1993; p 475. Miller, J. S.; Yee, G. T.; Manriquez, J. M.; Epstein, A. J. In *Conjugated Polymers and Related Materials: The Interconnection of Chemical and Electronic Structure*; Salaneck, W. R., Lündstrom, I., Rånby, B., Eds.; p 461.

[9] Miller, J. S.; Epstein, A. J. Submitted for publication.

[10] Beck, W.; Schlodder, R.; Lecher, K. H. *J. Organomet. Chem.* **1973**, *54*, 303.

[11] Schlodder, R.; Ibers, J. A. *Inorg. Chem.* **1974**, *13*, 2870.

[12] [(Ph$_3$P)$_2$(OC)Ir]$_2$[TCNE] was prepared from addition of 2 equiv of Ir^I complex (in THF) to an solution of [TCNE]$^{2-}$ freshly prepared from 2 equiv of NaNp and TCNE in THF.

[13] **Crystal Data for 1**: C$_{82}$H$_{63}$Ir$_2$N$_5$O$_2$P$_4$, M_r = 1658.73, yellow plate crystal (~0.04 × 0.25 × 0.33 mm), triclinic space group $P\bar{1}$ with a = 9.198(2) Å, b = 33.196(3), c = 11.848(1) Å, α = 90.16(1)°, β = 109.49(1)°, γ = 89.89(1)°, V = 1658.73 Å^3, Z = 2, d_{calcd} = 1.615 g cm^{-3}, μ(Mo Kα) = 40.27 cm^{-1}, 7522 independent reflections (1.2 < 2θ < 48.0, ω scan, T = –70 °C, R = 0.032, R_w = 0.029) were measured on Enraf-Nonius CAD4 diffractometer using graphite monochromated Mo Kα radiation (λ = 0.710 73 Å).

[14] Dixon, D. A.; Miller, J. S. *J. Am. Chem. Soc.* **1987**, *109*, 3656.

[15] Miller, J. S.; Calabrese, J. C.; Rommelmann, H.; Chittapeddi, S.; Zhang, J. H.; Reiff, W. M.; Epstein, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 769.

[16] Braunwarth, H.; Huttner, G.; Zsolnai, L. *J. Organomet. Chem.* **1989**, *372*, C23.

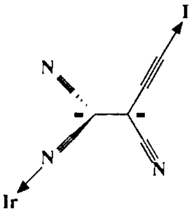
[17] (a) Bruce, M. I.; Wallis, R. C.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1981**, 2205. (b) Little, R. G.; Pautler, D.; Coppins, P. *Acta Crystallogr. B* **1971**, *37*, 1493.

0020-1669/93/1332-0377$04.00/0

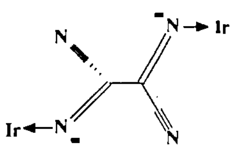
Table I. X-ray Crystallographically Determined Bond Lengths and Angles in $[TCNE]^n$ (n = 0, 1-, 2-)

	TCNE	π-$[TCNE]^{\bullet -}$	μ_2-$[TCNE]^{\bullet -}$	$[TCNE]^{2-}$	μ_2-$[TCNE]^{2-}$	μ_2-$[C_4(CN)_6]^{2-}$
cation		$[Fe(C_5Me_5)_2]^{\bullet +}$	$[MnTPP]^+$	$[Co(C_5Me_5)_2]^+$	$[Ir(CO)(PPh_3)_2]^+$	$[Rh(CO)(PPh_3)_2]^+$
TCNE sym	D_{2h}	D_{2h}	D_{2h}	D_{2d}		
temp, °C	25	−30	−100	−50	−70	
C—C, Å	1.344 (4)	1.392 (9)	1.369 (10)	1.49 (2)	1.478 (8)	1.449
C—CN, Å	1.439 (2)	1.417 (2)	1.434	1.392 (8)	1.417	1.432
C—CNM, Å			1.436		1.371	1.405
C≡N, Å	1.153 (2)	1.140 (4)	1.122	1.166 (3)	1.149	1.14
C≡NM, Å			1.137		1.164	1.153
C—C≡N, deg	178.2 (1)	179.9	175.7	177.6	176.9	176.9
C—C≡NM, deg			176.0		176.7	179.0
M—N≡C, deg			148.1		175.0	168.8
NC—C—CN, deg	115.6 (1)	117.7	119.5	117.1	118.8	117.1
$[(NC)_2C]_2$ dihedral angle, deg			1.9	87.1	67.2	20.0
R_w, %	3.5	5.4	5.9	8.3	2.9	8.6
$\nu_{C\equiv N}$, cm^{-1}	2259 s, 2221 m	2183 s, 2144 s	2187 m, 2139 m, 2126 s	2104 s, 2069 s	2176 m, 2097 s	
ref	17b	15	5	13	this work	11

$[MnTPP]^+[TCNE]^{\bullet -}$ (148.1°).[5] The linear Ir—N≡C angle is consistent with the anion charges being localized in orthogonal p-orbitals on the central C—C carbons, **3**, not **4**. The IrN≡C distances are essentially equivalent (i.e., ±0.015 Å) to the N≡C distances.



3



4

The $\nu_{C\equiv N}$ vibrational spectra of $[(Ph_3P)_2(OC)Ir]_2[TCNE]$ has absorptions at 2176 m and 2097 vs cm^{-1}. These are significantly blue-shifted by 72 and 28 cm^{-1}, respectively, from that reported for the isolated $[TCNE]^{2-}$.[14] Similar shifts (15–45 cm^{-1}) in the $\nu_{C\equiv N}$ stretching frequency are observed upon coordination of the weakly antibonding nitrogen lone pair of electrons of acetonitrile to metals.[18] The observed values are the closest to the values of 2188 and 2099 cm^{-1} reported for the $V[TCNE]_x{\cdot}yCH_2Cl_2$ room-temperature magnet[7,8] and thus suggests that $[TCNE]^{2-}$ may be present.

Acknowledgment. G.T.Y. and J.S.M. gratefully acknowledge the support from the Department of Energy, Division of Materials Science, Grant. No. DE-FG02-86ER45271.A000. We also appreciate the crystallographic expertise supplied by W. Marshall (Du Pont CRD).

Supplementary Material Available: An atom labeling figure as well as tables of crystallographic data, fractional coordinates/anisotropic thermal parameters, hydrogen atom parameters, general temperature factors, bond distances, bond angles and intermolecular distances (19 pages). Ordering information is given on any current masthead page.

---

[18] Endres, H. In *Comprehensive Coordination Chemistry*, Wilkinson, G., Ed.; Pergamon Press: Oxford, UK, 1987; p 264.