4686 Organometallics **1994,** *13,* 4686−4688

Synthesis and X-ray Crystal Structure of a Novel Iron Nitrosyl Complex, $Fe(NO)_2PPh_3(\eta^2\text{-}TCNE)$†

Lijuan Li,* Gary D. Enright, and Keith F. Preston

Steacie Institute for Molecular Sciences, National Research Council of Canada,
Ottawa, Ontario, Canada K1A 0R6

Received August 29, 1994®

Summary: The reaction of $Fe(NO)_2(CO)PPh_3$ *with TCNE (tetracyanoethylene) yields a novel iron dinitrosyl complex,* $Fe(NO)_2PPh_3(\eta^2\text{-}TCNE)$. *Its X-ray crystal structure shows that a TCNE molecule is π-bonded to the metal atom.*

From both chemical and biological points of view, transition-metal complexes containing nitric oxide have attracted considerable interest recently. Spectroscopic evidence would appear to implicate radicals of the "$Fe(NO)_2{}^{+}$" type in a variety of processes ranging from polymerization to carcinogenesis.[1] In biological systems, iron dinitrosyl complexes can be generated *in vitro* and *in vivo* by nitric oxide attack on naturally occurring [2Fe−2S] and [4Fe−4S] clusters in iron-sulfur proteins.[2] It has been demonstrated that these iron dinitrosyl complexes are related to the antibotulinal activity of nitrite ion.[1] The catalytic activity of iron dinitrosyl complexes has been known for more than two decades. Maxfield first reported that they were good catalysts for the stepwise conversion of 1,3-butadiene to 4-vinylcyclohexene.[3,4] They also efficiently catalyze the polymerization of styrene[5] and the oligomerization of acrylonitrile.[6] In 1987, Gadd *et al.*[7] used infrared spectroscopy to study the UV photolysis of $Fe(NO)_2(CO)_2$ in the presence of 1,3-butadiene in liquid xenon. They observed the replacement of one and two CO's by η^2- and/or η^4-bonded olefin at low temperature. They proposed that the dimerization of butadiene might occur *via* the intermediacy of $Fe(NO)_2(\eta^2\text{-}C_4H_8)(\eta^4\text{-}C_4H_8)$, where one NO is linear and one is bent. However, these complexes of olefins bonded to metal nitrosyls were not stable: they started to decompose at −50 °C. Up until now, no stable compound containing an olefin π-bonded to the iron dinitrosyl has been reported, yet they are clearly important intermediates implicated in catalysis by iron dinitrosyl complexes.

In the course of investigating the electronic structure of certain paramagnetic iron-nitrosyl complexes, we found that mixing equimolar amounts of $Fe(NO)_2(CO)PPh_3$ and TCNE in diethyl ether (10^{-3} M in each solute) resulted in the formation of orange crystals in a sealed EPR tube in a short space of time. This complex can also be synthesized by stirring equimolar amounts of $Fe(NO)_2(CO)PPh_3$ and TCNE in diethyl ether in a dry box.[8] The yellowish orange precipitate was formed in about 1 h in 70% yield.[9,10]

The X-ray crystal structure of the new complex is shown in Figure 1.[16] The iron is coordinated to two nitrosyls, to a triphenylphosphine, and to the C=C double bond of the TCNE. Both NO's are linear with one of the Fe−N−O angles close to 180° (178.0(5)°) and the other substantially less than 180° (165.8(5)°). The N1−Fe−N2 angle of 118.9° is similar to that found[11] in other iron dinitrosyl complexes, such as $Fe(NO)_2I_2$ (114°), $[Fe(NO)_2(SPh)_2]^-$ (117.4°), and $Fe(NO_2)(PPh_3)Cl$ (115.5°). The double bond of the π-bonded TCNE is 1.473(9) Å, which is significantly longer than in both free TCNE ($d_{C=C}$ = 1.317 Å) and $TCNE^-$ ($d_{C=C}$ = 1.392 Å).[12] The TCNE ligand is clearly not planar: the four CN groups are bent an average of 14.7° away from the plane containing C1=C2 that is perpendicular to the FeC1C2 plane. This is consistent with the structures of many olefin complexes in which the olefin loses planarity upon coordination.

Each asymmetric unit contains a partially occupied (0.95) solvent molecule that exhibits large-amplitude torsional motion leading to large thermal ellipsoids (Figure 1) for the solvent atoms and shortened inferred C−C bond distances. The oxygen atom of the ether solvent molecule faces the TCNE, and the bisector of the COC angle intersects the midpoint of the TCNE double bond and the Fe atom. Thus, the oxygen atom appears to donate its lone pair to the electronegative TCNE to stabilize the structure. However, there is no direct bonding, since the distance from oxygen to C1 and C2 is 3.24 Å, which corresponds to the sum of their Van der Waals radii.

In the crystal packing, along the *a* and *b* axes, the triphenylphosphine and TCNE alternate their positions, and they are not aligned along the *c* axis. The triphen-

---

† NRCC No. 37289.

® Abstract published in *Advance ACS Abstracts,* November 15, 1994.

[1] Glidewell, C., *Chem. Br.* **1990,** *26*(2), 137.

[2] Vanin, A. F.; Men'shikov, G. B.; Moroz, I. A.; Mordvintcev, P. I.; Serezhenkov, V. A.; Burbaev, D. S. *Biochim. Biophys. Acta* **1992,** *1135,* 275.

[3] Maxfield, P. L. U.S. Patent 3 377 397 (Oct 22, 1965).

[4] Candlin, J. P.; Janes, W. H. *J. Chem. Soc. C* **1968,** 1856.

[5] (a) Ballivet-Tkatchenko, D.; Riveccie, M.; El-Murr, N. *J. Am. Chem. Soc.* **1979,** *101,* 2763. (b) Ballivet-Tkatchenko, D.; Billard, C.; Revillon, A. *J. Polym. Sci.* **1981,** *19,* 1697.

[6] Ballivet, D. *J. Organomet. Chem.* **1977,** *124,* C9.

[7] Gadd, G. E.; Poliakoff, M.; Turner, J. J. *Organometallics* **1987,** *6,* 391.

[8] All of the solvents were dried according to standard procedures.

[9] Fast-atom bombardment mass spectrometry studies show the presence of the molecular ion ($(m + H)/e$ 507) and the fragment ions with m/e 378 (loss of TCNE), 348 and 318 (loss of NO's), and 263 (loss of Fe).

[10] Anal. Calcd for $C_{24}H_{15}N_6O_2FeP$: C, 56.92; H, 2.96; N, 16.6. Found: C, 59.33; H, 2.62; N, 17.40.

[11] Bryar, T. R.; Eaton, D. R. *Can. J. Chem.* **1992,** *70,* 1917.

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

0276-7333/94/2313-4686$04.50/0 Published 1994 by the American Chemical Society

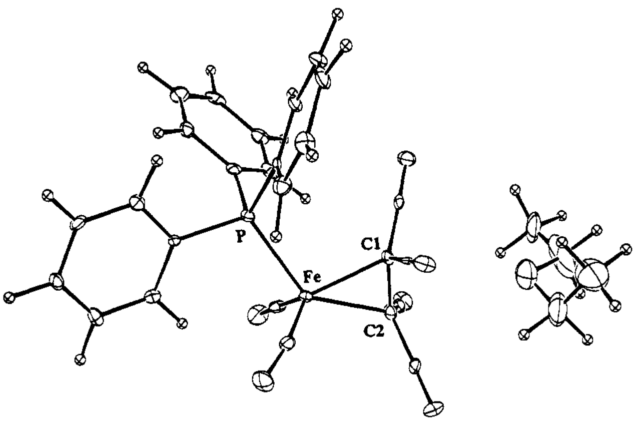


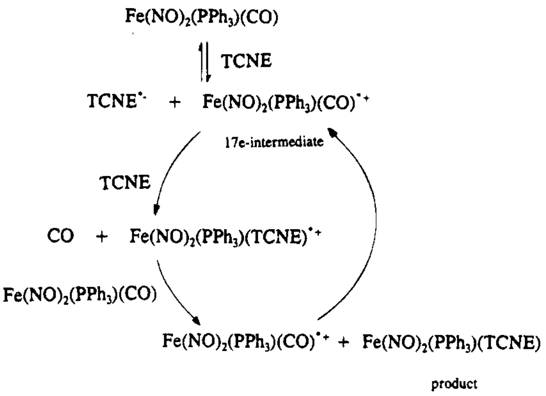
Figure 1. ORTEP[15] diagram of the crystal structure of $Fe(NO)_2PPh_3(\eta^2\text{-}TCNE)$ and solvent molecule. Selected bond lengths and bond angles: Fe–P = 2.296(2) Å; Fe–N = 1.657(6) and 1.665(6) Å; Fe–C1/Fe–C2 = 2.029(7)/2.101(6) Å; C1–C2 = 1.473(9) Å; N1–Fe–N2 = 118.9°; Fe–N1–O1 = 178.0(5)°; Fe–N2–O2 = 165.8(5)°.

ylphosphines are twisted away from each other due to steric hindrance.

The ^{13}C NMR spectrum of this complex was recorded at 100.6 MHz at room temperature in CD_2Cl_2. Phenyl ring resonances were found for C_{meta} at 133.66 ppm (doublet, J_{C-P} = 11.1 Hz), C_{para} at 132.98 ppm (doublet, J_{C-P} = 2.8 Hz), C_{ortho} at 130.15 ppm (doublet, J_{C-P} = 11.1 Hz), and C_{ipso} at 127.35 ppm (doublet, J_{C-P} = 49.9 Hz). The four cyano carbons appeared in pairs (113.95 ppm, doublet, J_{C-P} = 3.4 Hz; 113.77 ppm, doublet, J_{C-P} = 2.4 Hz), which is in agreement with the solid-state structure, where the cyano carbons are equivalent in pairs when triphenylphosphine rotation is fast. The two ethylene carbons were also magnetically distinct with chemical shifts of 29.69 ppm (doublet, J_{C-P} = 11.1 Hz, the one close to phosphorus) and 29.94 ppm (doublet, J_{C-P} = 4.0 Hz, the one further away from phosphorus). They are both shifted to higher field compared with free TCNE, in which the ethylene carbons resonate at 112.6 ppm in CH_2Cl_2. A ^{13}C chemical shift of ~30 ppm is more appropriate for saturated carbon than unsaturated carbon, indicating that the ethylene carbons of this iron–nitrosyl complex approach sp^3-hybridized character and depart significantly from the sp^2-hybridized character in planar TCNE. This NMR observation is entirely consistent with the crystal structure determination, which showed a C=C distance in the π-bonded TCNE significantly longer than a normal double bond and a TCNE group that was distinctly nonplanar.

The IR spectrum in solid KBr shows two strong absorbances for NO stretches at 1835.6 and 1790.2 cm^{-1}. These modes are shifted to higher frequencies compared with the starting material $Fe(NO)_2(CO)PPh_3$, in which the two NO stretches are at 1766.0 and 1718.7 cm^{-1} and the CO stretch is at 2007.9 cm^{-1}. The CN stretch of the complex at 2224.3 cm^{-1} falls between the values for free TCNE (2262 and 2222 cm^{-1}) and $TCNE^-$ (2183 and 2144 cm^{-1}). We associate the lower CN stretching frequency in the complex with a back-donation of filled metal d orbitals to the vacant π^*-antibonding orbital of TCNE, which weakens the CN bonds. Such back-donation to the TCNE renders the metal atom partially positive, thereby reducing back-donation from the metal to the NO bond and shifting the NO stretches to higher frequencies.

Scheme 1. Suggested Reaction Pathway: An Electron Transfer Autocatalysis Mechanism



Generally, carbonyl substitution reactions are slow. To substitute one CO in $Fe(NO)_2(CO)_2$ usually calls for stirring overnight, and replacing a second CO requires heating to 85 °C for 16 h.[13] However, in this reaction, the substitution of CO by TCNE is complete in 1–2 h at room temperature. We monitored the reaction by EPR spectroscopy and observed both $TCNE^-$ and $Fe(NO)_2(PPh_3)L^+$ (L may be CO or solvent) radicals[14] upon mixing of the starting materials (the EPR spectrum shows a triplet of doublets which results from coupling to the phosphorus and two equivalent ^{15}N). The observation of the EPR spectra suggests a free-radical mechanism involving a 17-electron intermediate. We speculate that the rapidity of this reaction may be due to the participation of free radicals, as in the "electron transfer autocatalytic" mechanism proposed in Scheme 1.

The new complex is diamagnetic in the solid state. However, in solution, especially in polar solvents, TCNE dissociates from the complex at room temperature to yield paramagnetic products. One of them is the $TCNE^-$ radical anion, which gives a 9-line EPR spectrum due to interactions of the unpaired electron with four equivalent nitrogens (a_{iso} = 1.56 G, g_{iso} = 2.002): The more polar the solvent, the stronger the signal of $TCNE^-$ observed. In THF, other complex EPR signals are observed that have thus far defied analysis. We tentatively associate these signals with iron nitrosyl cluster cations. The isotropic ^{31}P hyperfine interaction

---

(13) McBride, D. W.; Stafford, S. L.; Stone, F. G. A. *Inorg. Chem.* **1962,** *1,* 386.

(14) Li, L.; Morton, J. R.; Preston, K. F. Unpublished work.

(15) Johnson, C. K. ORTEP–A Fortran Thermal Ellipsoid Plot Program; Technical Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(16) The crystal structure was determined using an orange crystal of dimensions 0.35 × 0.30 × 0.14 mm. The intensity data were collected at 115 K on an Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.7930$ Å). Crystal data: $FePO_3N_6C_{28}H_{25}$, monoclinic, space group $P2_1/c$, $a = 11.2177(12)$ Å, $b = 16.668(3)$ Å, $c = 15.200(5)$ Å, $\beta = 90.72(3)°$, $V = 2841.8(10)$ Å^3, $Z = 4$, $D_c = 1.350$ g cm^{-3}, μ(Mo Kα) = 0.62 mm^{-1}, $R = 0.057$, and $R_w = 0.055$ (GOF = 1.32), for 2395 reflections with $1.5 < \theta < 25°$ and $I > 2.5\sigma(I)$. H atoms were located and fixed in calculated positions. Atomic coordinates, bond distances and angles, and thermal parameters for independent molecules of the asymmetric unit have been deposited at the Cambridge Crystallographic Data Centre. See the Notice to Authors in the January 1993 issue of *Organometallics.*

(50.6 G) and *g* value (2.035) indicate that these species are closely related to $Fe(NO)_2^+$. Further studies are underway to establish the detailed mechanism and the nature of the products.

Acknowledgment. We wish to thank Drs. D. D. M. Wayner and J. R. Morton for helpful discussions, Mr. R. Dutrisac for technical assistance, and the National Research Council of Canada for a Research Associateship (L.L.).

Supplementary Material Available: Tables of crystal data and refinement details, bond lengths, bond angles, atomic coordinates, and thermal parameters for $Fe(NO)_2PPh_3(\eta^2$-TCNE) (6 pages). Ordering information is given on any current masthead page.

OM940689E