

Novel and Stable Metal–Metal-Bonded Diruthenium(I) Complexes Containing TCNX^{0/+} in Both the Inner and the Outer Coordination Sphere (TCNX = TCNE, TCNQ). A Combined EPR/ENDOR-, UV/Vis/Near-IR-, and IR-Spectroscopic and Electrochemical Investigation

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Reaction of the diphosphazane-bridged diruthenium derivatives $\text{Ru}_2(\mu\text{-CO})(\text{CO})_4[\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2]_2$ ($\text{R} = \text{Me}, \text{tPr}$) with the electron acceptors TCNX ($\text{X} = \text{Q}, \text{E}$) affords products of the type $\{\text{Ru}_2(\text{CO})_5[\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2]_2(\eta^1\text{-TCNX})\}(\text{TCNX})$ containing a TCNX radical anion in both the inner and outer coordination sphere of the cation. The contribution of the coordinated TCNX^{•-} to the EPR/ENDOR and UV/vis/near-IR spectra of these salts is partly obscured by that of the external, completely dissociated D_{2h} -symmetric TCNX^{•-}, but the infrared vibrational spectra and, in particular, the cyclic voltammograms show clearly the presence of both coordinated and noncoordinated species. Four distinct and reversible waves appear in benzonitrile; two correspond to the TCNX^{0/-} and TCNX⁻²⁻ couples of the external TCNX, while the other pair, shifted by ca. 0.3 V to more positive potentials because of rather weak $\text{Ru} \rightarrow \text{TCNX} \pi$ back-donation, are readily assigned to the corresponding redox couples of the coordinated TCNX. The external TCNQ^{•-} anion of the TCNQ salts is readily exchanged for the diamagnetic tetraphenylborate anion to give compounds of the type $\{\text{Ru}_2(\text{CO})_5[\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2]_2(\eta^1\text{-TCNQ})\}(\text{BPh}_4)$ ($\text{R} = \text{Me}, \text{tPr}$), thus enabling UV/vis/near-IR, IR, and EPR spectra of the coordinated TCNQ^{•-} to be recorded in CH_2Cl_2 without interference from the external TCNQ^{•-} anion; the IR and EPR data confirm the low symmetry of the η^1 -bound TCNQ^{•-}. With the aid of HMO/McLachlan perturbation calculations and ENDOR measurements it proved possible, for the first time, to record and reproduce EPR spectra of a coordinated TCNQ^{•-} anion; the ¹H and ¹⁴N hyperfine coupling constants used to simulate the EPR spectra fit the pattern calculated for a TCNQ^{•-} bonded in the η^1 -mode to one metal center. Replacement of the external TCNE^{•-} in the TCNE salts by a diamagnetic anion could not be achieved, but since the external TCNE^{•-} is more easily oxidized than bound TCNE^{•-}, selective oxidation of the former in situ to diamagnetic neutral TCNE could be accomplished, thus allowing EPR spectra of the coordinated TCNE^{•-} to be recorded in CH_2Cl_2 without interference from external TCNE^{•-}. Successful reproductions of the highly resolved EPR spectra showed that, like TCNQ^{•-}, TCNE^{•-} is bonded in the η^1 -mode to one metal center. In situ oxidation of $\{\text{Ru}_2(\text{CO})_5[\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2]_2(\eta^1\text{-TCNX})\}^+$ ($\text{R} = \text{Me}, \text{tPr}$) affords the completely oxidized dications containing a neutral coordinated TCNX ligand; these dications, as well as the reduced species $\{\text{Ru}_2(\text{CO})_5[\mu\text{-(tPrO)}_2\text{PN}(\text{Et})\text{P}(\text{O}^i\text{Pr})_2]_2(\eta^1\text{-TCNQ})\}$, were characterized by UV/vis/near-IR spectroscopy.

Introduction

The inorganic and organometallic coordination chemistry of tetracyanoethylene (TCNE)¹ and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) continues to be of considerable interest for several reasons: (i) As strong π acceptors, these TCNX (TCNX = TCNE, TCNQ) ligands give rise to metal complexes in which the ligand may be coordinated in different oxidation states, i.e. as neutral,² radical anionic,³ and dianionic molecules.⁴ (ii) As unsaturated polynitriles, TCNE and TCNQ can bind metals

through olefinic bonds^{2a-c,4} or through one or more^{2d,3c,5} of the nitrile N lone pairs.^{3,6} (iii) Intermolecular association, valence fluctuation, and spin (de)coupling can lead to solid materials exhibiting unusual conducting, optical, or magnetic properties.⁷

Of late the coordination chemistry of TCNE and TCNQ has been extended to their reactions with dinuclear species and, in particular, to their reactions with multiply bonded systems. The two examples reported to date are the reaction of TCNE with $\text{Mo}_2(\text{C}_{22}\text{H}_{22}\text{N}_4)_2$ ⁸ and the reaction of TCNQ with $\text{Re}_2\text{Cl}_4(\text{dppm})_2$

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(1) Fatiadi, A. J. *Synthesis* 1986, 249; 1987, 959.

(2) (a) Herberhold, M. *Angew. Chem.* 1972, 84, 773. Herberhold, M. *Angew. Chem.* 1968, 80, 314; *Angew. Chem., Int. Ed. Engl.* 1968, 7, 305.

(b) Olbrich-Deussner, B.; Gross, R.; Kaim, W. *J. Organomet. Chem.* 1989, 366, 155. (c) Stufkens, D. J.; Snoeck, T. L.; Kaim, W.; Roth, T.; Olbrich-Deussner, B. *J. Organomet. Chem.* 1991, 409, 189. (d) Sacher, W.; Nagel, U.; Beck, W. *Chem. Ber.* 1987, 120, 895.

(3) (a) Rettig, M. F.; Wing, R. M. *Inorg. Chem.* 1969, 8, 2685. (b) Olbrich-Deussner, B.; Kaim, W.; Gross-Lannert, R. *Inorg. Chem.* 1989, 28, 3113. (c) Gross-Lannert, R.; Kaim, W.; Olbrich-Deussner, B. *Inorg. Chem.* 1990, 29, 5046. (d) Braunwarth, H.; Huttner, G.; Zsolnai, L. *J. Organomet. Chem.* 1989, 372, C23.

(4) Baddley, W. H. *Inorg. Chim. Acta Rev.* 1968, 2, 7.

(5) (a) Crumbliss, A. L.; Basolo, F. *Inorg. Chem.* 1971, 10, 1676. (b) Beck, W.; Schlodder, R.; Lechler, K. H. *J. Organomet. Chem.* 1973, 54, 303.

(c) Moers, F. G.; Langhout, J. P. *J. Inorg. Nucl. Chem.* 1977, 39, 591.

(d) Amer, S. I.; Dasgupta, T. P.; Henry, P. M. *Inorg. Chem.* 1983, 22, 1970.

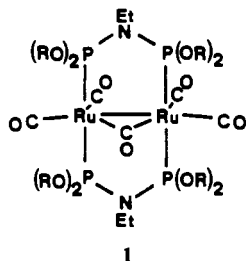
(6) Humphrey, D. G.; Fallon, G. D.; Murray, K. S. *J. Chem. Soc., Chem. Commun.* 1988, 1356.

(7) (a) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Acc. Chem. Res.* 1988, 21, 114. (b) 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. (c) Dixon, D. A.; Miller, J. S. *J. Am. Chem. Soc.* 1987, 109, 3656. (d) Yee, G. T.; Manriquez, J. M.; Dixon, D. A.; McLean, R. S.; Groski, D. M.; Flippen, R. B.; Narayan, K. S.; Epstein, A. J.; Miller, J. S. *Adv. Mater.* 1991, 3, 309. (e) Manriquez, J. M.; Yee, G. T.; McLean, R. S.; Epstein, A. J.; Miller, J. S. *Science* 1991, 252, 1415.

(8) Giraudon, J. M.; Guerschais, J. E.; Sala-Pala, J.; Toupet, L. *J. Chem. Soc., Chem. Commun.* 1988, 921.

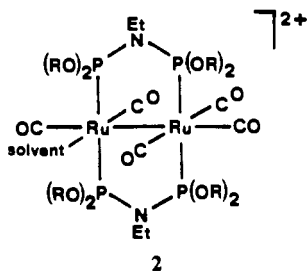
to give $[\text{Re}_2\text{Cl}_4(\text{dppm})_2](\mu\text{-TCNQ})$;⁹ in the latter complex the two rhenium atoms are bridged by a TCNQ molecule via opposite nitrile groups as confirmed crystallographically. Another example of a structurally characterized dinuclear complex $[\text{Ru}(\text{PPh}_3)_2(\text{TCNQ})]_2$ has the nonbonded metal atoms bridged by two TCNQ ligands via opposite nitrile groups.¹⁰ Also of considerable interest are the reactions of electron-rich organometallic donors with TCNE or TCNQ to give "charge-transfer" salts in which the $\text{TCNX}^{\cdot-}$ anion is *not* coordinated to the metal atom(s). Many of these salts have material properties which are dependent on the extent of charge transfer and on the arrangement of the donor cations and the $\text{TCNX}^{\cdot-}$ anions in the solid.^{7,11}

In this paper we report the reactions of the electron-rich diphosphazane-bridged derivatives of diruthenium nonacarbonyl $\text{Ru}_2(\mu\text{-CO})(\text{CO})_4[\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2]_2$ (**1**)¹² ($\text{R} = \text{Me}, \text{}^i\text{Pr}$) with



1

TCNE and TCNQ. Electrochemical studies of complexes **1** show that their oxidation potentials are smaller than the potentials required to reduce either TCNE or TCNQ, and for this reason, we expected them to participate in spontaneous electron-transfer reactions with the TCNX molecules.¹³ The electrochemical studies also showed that oxidation of complexes **1** in a variety of solvents leads to the formation of dicationic solvento species of the type $\{\text{Ru}_2(\text{CO})_5[\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2]_2(\text{solvent})\}^{2+}$ (**2**)



2

(solvent = benzonitrile, acetone, dichloromethane) as the end product of the oxidation process.¹³ Similarly, oxidation of complexes **1** by silver salts affords the dicationic solvento species **2** as confirmed by an X-ray crystal structure determination of $\{\text{Ru}_2(\text{CO})_5[\mu\text{-(}^i\text{PrO)}_2\text{PN}(\text{Et})\text{P}(\text{O}^i\text{Pr})_2]_2(\eta^1\text{-PhCN})\}(\text{SbF}_6)_2$.¹⁴ Subsequent chemical studies showed that the solvent molecule in **2** is readily replaced by neutral and anionic nucleophiles,¹⁴ and thus a further expectation was that a $\text{TCNX}^{\cdot-}$ radical anion formed in the initial electron-transfer reaction of **1** with TCNX would replace the coordinated solvent molecule. The presence of two positive charges but only one open coordination site for

a nitrile group leads to the possibility of having an additional $\text{TCNX}^{\cdot-}$ anion radical as the external counterion and thus to having both η^1 -coordinated $\text{TCNX}^{\cdot-}$ and "free" $\text{TCNX}^{\cdot-}$ in the same compound, i.e. $\text{TCNX}^{\cdot-}$ in both the inner and outer coordination sphere of the dication. The details of the synthesis of the compounds $\{\text{Ru}_2(\text{CO})_5[\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2]_2(\eta^1\text{-TCNX})\}(\text{TCNX})$ from the reaction of **1** with either TCNE or TCNQ and the characterization of these and the related compounds $\{\text{Ru}_2(\text{CO})_5[\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2]_2(\eta^1\text{-TCNQ})\}(\text{BPh}_4)$ are reported here ($\text{R} = \text{Me}, \text{}^i\text{Pr}$). Unfortunately, despite many and determined attempts using a variety of solvent systems and crystallization techniques, it was not possible to grow single crystals of any of the isolated TCNX salts; as a result we have had to rely on IR, UV/vis/near-IR, and EPR/ENDOR spectroscopy and cyclic voltammetry to characterize the new compounds. Because of the lability of the TCNE complexes, it was not possible to isolate a complex in which the external $\text{TCNE}^{\cdot-}$ was exchanged for a diamagnetic counterion; however, in situ generation procedures allowed us to study such species and a number of interesting oxidation states by EPR and UV/vis spectroscopy. A preliminary report of aspects of this work has appeared.¹⁵

Experimental Section

All chemical reactions and operations were performed under an argon atmosphere by employing standard vacuum-line and Schlenk techniques. Solvents were freshly distilled under argon or nitrogen prior to use: dichloromethane and benzonitrile from P_2O_{10} ; toluene, diethyl ether, light petroleum ether (60–80 °C), and tetrahydrofuran from Na or K. TCNE was purchased from Merck Chemical Co., and TCNQ and NaBPh_4 were purchased from Sigma Chemical Co.; all were used as received. The starting materials $\text{Ru}_2(\mu\text{-CO})(\text{CO})_4[\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2]_2$ ($\text{R} = \text{Me}, \text{}^i\text{Pr}$) were prepared according to the literature procedure.¹²

$\{\text{Ru}_2(\text{CO})_5[\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2]_2(\eta^1\text{-TCNX})\}(\text{TCNX})$ ($\text{R} = \text{Me}, \text{}^i\text{Pr}$; $\text{TCNX} = \text{TCNQ}, \text{TCNE}$). A toluene solution (20 mL) of 0.20 g of $\text{Ru}_2(\mu\text{-CO})(\text{CO})_4[\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2]_2$ ($\text{R} = \text{Me}, \text{}^i\text{Pr}$) was added dropwise to a stirred solution of ca. 2.2 mol equiv of TCNX in 30 mL of toluene at room temperature. A green ($\text{TCNX} = \text{TCNQ}$) or yellow ($\text{TCNX} = \text{TCNE}$) precipitate formed immediately, which was filtered from the solution, washed with diethyl ether, and dried in vacuo to give the product in essentially quantitative yield. The green TCNQ salts ($\text{R} = \text{Me}, \text{}^i\text{Pr}$) were purified further by crystallization from CH_2Cl_2 /light petroleum ether (60–80 °C) to give dark green microcrystalline solids. The yellow TCNE salts ($\text{R} = \text{Me}, \text{}^i\text{Pr}$) were analytically pure, and in fact, attempts to crystallize these salts from CH_2Cl_2 /light petroleum ether resulted in decomposition to brown materials. Anal. Calcd for (i) $\text{R} = \text{Me}$, $\text{TCNX} = \text{TCNQ}$, $\text{C}_{41}\text{H}_{42}\text{N}_{10}\text{O}_{13}\text{P}_4\text{Ru}_2$ ($M_r = 1208.89$): C, 40.73; H, 3.50; N, 11.58. Found: C, 40.34; H, 3.25; N, 11.42. Calcd for (ii) $\text{R} = \text{}^i\text{Pr}$, $\text{TCNX} = \text{TCNQ}$, $\text{C}_{57}\text{H}_{74}\text{N}_{10}\text{O}_{13}\text{P}_4\text{Ru}_2$ ($M_r = 1433.59$): C, 47.75; H, 5.22; N, 9.77. Found: C, 47.83; H, 5.23; N, 9.92. Calcd for (iii) $\text{R} = \text{Me}$, $\text{TCNX} = \text{TCNE}$, $\text{C}_{29}\text{H}_{34}\text{N}_{10}\text{O}_{13}\text{P}_4\text{Ru}_2$ ($M_r = 1056.70$): C, 32.96; H, 3.24; N, 13.25. Found: C, 32.90; H, 3.41; N, 13.15. Calcd for (iv) $\text{R} = \text{}^i\text{Pr}$, $\text{TCNX} = \text{TCNE}$, $\text{C}_{45}\text{H}_{66}\text{N}_{10}\text{O}_{13}\text{P}_4\text{Ru}_2$ ($M_r = 1286.13$): C, 42.02; H, 5.17; N, 10.89. Found: C, 42.31; H, 5.03; N, 11.31.

$\{\text{Ru}_2(\text{CO})_5[\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2]_2(\eta^1\text{-TCNQ})\}(\text{BPh}_4)$ ($\text{R} = \text{Me}, \text{}^i\text{Pr}$). Solid NaBPh_4 (ca. 0.30 g) was added to a stirred solution of 0.20 g of $[\text{Ru}_2(\text{CO})_5[\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2]_2(\eta^1\text{-TCNQ})\}(\text{TCNQ})$ ($\text{R} = \text{Me}, \text{}^i\text{Pr}$) in 20 mL of THF at room temperature. The blue precipitate of $\text{Na}(\text{TCNQ})$ which formed immediately was filtered from the green solution. The filtrate was concentrated under vacuum to half its original volume and light petroleum ether added dropwise until a blue-green precipitate of the crude product had formed. Following separation by filtration, the crude products were purified by repeated crystallization from CH_2Cl_2 /light petroleum to give bright-green microcrystalline materials. Yields of pure products were ca. 40%. Anal. Calcd for (i) $\text{R} = \text{Me}$, $\text{C}_{53}\text{H}_{58}\text{BN}_6\text{O}_{13}\text{P}_4\text{Ru}_2$ ($M_r = 1328.93$): C, 47.90; H, 4.40; N, 6.32. Found: C, 48.09; H, 4.65; N, 6.53. Calcd for (ii) $\text{R} = \text{}^i\text{Pr}$, $\text{C}_{69}\text{H}_{90}\text{BN}_6\text{O}_{13}\text{P}_4\text{Ru}_2$ ($M_r = 1553.36$): C, 53.35; H, 5.84; N, 5.41. Found: C, 53.32; H, 5.42; N, 5.13.

(9) Bartley, S. L.; Dunbar, K. R. *Angew. Chem.* **1991**, *103*, 447; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 448.

(10) Ballester, L.; Barral, M. C.; Gutierrez, A.; Jimenez-Aparicio, R.; Martinez-Muyo, J. M.; Perpignan, M. F.; Monge, M. A.; Ruiz-Valero, C. *J. Chem. Soc., Chem. Commun.* **1991**, 1396.

(11) Endres, H. In *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum Press: New York, 1983; Chapter 3, p 263. Green, M. L. H.; Qin, J.; O'Hare, D. *J. Organomet. Chem.* **1988**, *358*, 375.

(12) de Leeuw, G.; Field, J. S.; Haines, R. J.; McCulloch, B.; Meintjies, E.; Monberg, C.; Olivier, G. M.; Ramdial, P.; Sampson, C. N.; Sigwarth, B.; Steen, N. D. *J. Organomet. Chem.* **1984**, *275*, 99.

(13) Field, J. S.; Francis, A. M. A.; Haines, R. J.; Woollam, S. F. *J. Organomet. Chem.* **1991**, *412*, 383.

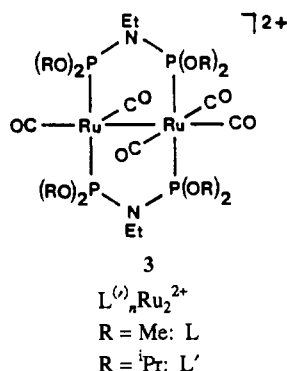
(14) Field, J. S.; Haines, R. J.; Honrath, B.; Sundermeyer, J.; Woollam, S. F. *J. Organomet. Chem.* **1990**, *395*, C9.

(15) Bell, S. E.; Field, J. S.; Haines, R. J.; Sundermeyer, J. *J. Organomet. Chem.* **1992**, *427*, C1.

Instrumentation. EPR/ENDOR: Bruker system ESP 300/A500 spectrometer in the X band. *g* factors were determined using a Bruker NMR ER035M gaussmeter and a HP 5350B microwave counter. IR: Perkin-Elmer 283 and 684 spectrometers. UV/vis/near-IR: Bruins Instruments Omega 10. Cyclic voltammetry: PAR system 173/175, three-electrode configuration with a platinum working electrode, Ag/AgCl reference, and platinum counter electrode. Ferrocene/ferrocenium (Fc/Fc⁺) was used as a pilot system. Hückel MO/McLachlan calculations of π spin populations were carried out using standard programs with conventional parameters $h_N = 1.0$ and $k_{C=N} = 2.0$.^{16a} EPR spectral simulations were performed using the modification of an available program.^{16b}

Results and Discussion

All the compounds synthesized and studied in this work derive from the coordinatively unsaturated fragment $\{\text{Ru}_2(\text{CO})_5[\mu-(\text{RO})_2\text{PN}(\text{Et})\text{P}(\text{OR})_2]_2\}^{2+}$ (3). As indicated by the structural



formula of 3, the fragment contains one vacant coordination site at one metal center. The following abbreviation for 3 will be used in the text and tables: $\{\text{Ru}_2(\text{CO})_5[\mu-(\text{RO})_2\text{PN}(\text{Et})\text{P}(\text{OR})_2]_2\}^{2+} = L^{(\prime)}\text{Ru}_2^{2+}$ (R = Me, ⁱPr). In order to distinguish between the two R groups used in this work, viz. Me and ⁱPr, abbreviations are used as follows: $L_n\text{Ru}_2^{2+}$ (R = Me); $L'_n\text{Ru}_2^{2+}$ (R = ⁱPr).

Synthetic and Electrochemical Studies. The course of the reaction of both TCNQ and TCNE with 1 (R = Me, ⁱPr) was found to be dependent on the choice of solvent and, in particular, on the order and rate of addition of the reactants. In order to obtain the desired salts $[L^{(\prime)}\text{Ru}_2(\eta^1\text{-TCNX})](\text{TCNX})$, it was essential to add a solution of the diruthenium complex slowly to a solution of the electron-acceptor ligand, the best solvent for reproducible results being toluene and the highest yields being obtained with a molar ratio of TCNX to 1 of slightly more than 2.

Slow addition of a toluene solution of 1 (R = Me, ⁱPr) to a solution of ca. 2.2 mol equiv of TCNQ in toluene led to the immediate formation of green precipitates, which, on crystallization from dichloromethane/light petroleum ether, afforded fine dark-green microcrystalline materials characterized as the 1:1 salts $\{\text{Ru}_2(\text{CO})_5[\mu-(\text{RO})_2\text{PN}(\text{Et})\text{P}(\text{OR})_2]_2(\eta^1\text{-TCNQ})\}(\text{TCNQ})$ (R = Me, ⁱPr). Figure 1a shows the cyclic voltammogram recorded in benzonitrile/0.1 M Bu₄NClO₄ of the R = Me compound. Four distinct, reversible one-electron waves are observed, two of which (I and IV) correspond to those of TCNQ itself (Table I), indicating the presence of both a coordinated and a noncoordinated TCNQ⁻ in the salt. With the aim of establishing unequivocally the presence of two different TCNQ⁻ species in these salts, they were reacted with an excess of sodium tetraphenylborate in THF to effect the replacement of the external TCNQ⁻ with the BPh₄⁻ anion. A dark-blue precipitate of Na-

Table I. Half-Wave Potentials $E_{1/2}$ (V) for TCNX (X = E, Q) and for the Diruthenium(I) Complexes of Their Radical Anions^a

compd	redox couple			
	$\eta^1\text{-TCNX}/\eta^1\text{-TCNX}^-$	TCNX/TCNX ⁻	$\eta^1\text{-TCNX}^-/\eta^1\text{-TCNX}^{2-}$	TCNX ⁻ /TCNX ²⁻
TCNE		-0.22		-1.29
$[\text{L}_n\text{Ru}_2(\text{TCNE})](\text{TCNE})$	0.11	-0.20	-0.83	$\sim -1.3^b$
$[\text{L}'_n\text{Ru}_2(\text{TCNE})](\text{TCNE})$	0.15	-0.20	-0.71	$\sim -1.3^b$
TCNQ		-0.23		-0.88
$[\text{L}_n\text{Ru}_2(\text{TCNQ})](\text{BPh}_4)$	0.04		-0.58	
$[\text{L}_n\text{Ru}_2(\text{TCNQ})](\text{TCNQ})$	0.05	-0.25	-0.61	-0.91
$[\text{L}'_n\text{Ru}_2(\text{TCNQ})](\text{BPh}_4)$	0.08		-0.57	
$[\text{L}'_n\text{Ru}_2(\text{TCNQ})](\text{TCNQ})$	0.07	-0.25	-0.58	-0.86

^a $E_{1/2} = (E_{pa} + E_{pc})/2$ referred to Fc/Fc⁺ measured in benzonitrile/0.1 M Bu₄NClO₄ at Pt, scan rate 200 mV/s, *T* = 298 K. ^b Wave not fully reversible.

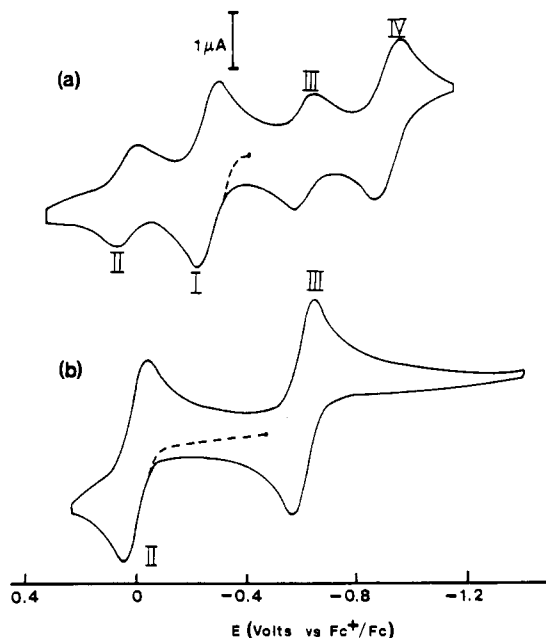


Figure 1. Cyclic voltammograms recorded in benzonitrile (0.1 M Bu₄NClO₄, 25 °C, 200 mV/s scan rate) at Pt of 10⁻³ M solutions of (a) $\{\text{Ru}_2(\text{CO})_5[\mu-(\text{MeO})_2\text{PN}(\text{Et})\text{P}(\text{OMe})_2]_2(\eta^1\text{-TCNQ})\}(\text{TCNQ})$ and (b) $\{\text{Ru}_2(\text{CO})_5[\mu-(\text{MeO})_2\text{PN}(\text{Et})\text{P}(\text{OMe})_2]_2(\eta^1\text{-TCNQ})\}(\text{BPh}_4)$.

(TCNQ) separated immediately from the green solutions, from which green solids characterized as $\{\text{Ru}_2(\text{CO})_5[\mu-(\text{RO})_2\text{PN}(\text{Et})\text{P}(\text{OR})_2]_2(\eta^1\text{-TCNQ})\}(\text{BPh}_4)$ could be isolated. The cyclic voltammogram of the R = Me salt in benzonitrile/0.1 M Bu₄NClO₄ is illustrated in Figure 1b. Only two waves are observed which correspond with waves II and III in the cyclic voltammogram of $[\text{L}_n\text{Ru}_2(\eta^1\text{-TCNQ})](\text{TCNQ})$ (Figure 1a and Table I). The separation between waves II and III is essentially the same as that between waves I and IV of TCNQ itself, an observation which strongly suggests that the former arise from redox processes associated with the coordinated TCNQ ligand rather than with the ruthenium atoms. On this basis, wave II is assigned to the $\eta^1\text{-TCNQ}/\eta^1\text{-TCNQ}^-$ couple and wave III to the $\eta^1\text{-TCNQ}^-/\eta^1\text{-TCNQ}^{2-}$ couple. Remarkably, these couples are shifted to even more positive potentials as compared to the equivalent couples for free TCNQ (Table I).

Slow addition of a toluene solution of 1 (R = Me, ⁱPr) to a solution of ca. 2.2 mol equiv of TCNE in toluene led to the immediate formation of yellow precipitates, isolated and characterized as analytically pure $\{\text{Ru}_2(\text{CO})_5[\mu-(\text{RO})_2\text{PN}(\text{Et})\text{P}(\text{OR})_2]_2(\eta^1\text{-TCNE})\}(\text{TCNE})$ (R = Me, ⁱPr). These salts are far less stable than their TCNQ counterparts, decomposing to a brown material even when only trace amounts of oxygen are present. This difference in stability is tentatively attributed to the better charge delocalization in the larger π system; however, in other cases where structurally analogous neutral TCNQ and TCNE

(16) (a) Calculated and experimental spin densities for anion radicals of TCNE and TCNQ: Rieger, P. H.; Bernal, I.; Fraenkel, G. K. *J. Am. Chem. Soc.* **1961**, *83*, 3918. Rieger, P. H.; Fraenkel, G. K. *J. Chem. Phys.* **1962**, *37*, 2795. (b) Oehler, V. M.; Janzen, E. G. *Can. J. Chem.* **1982**, *60*, 1542.

Table II. Infrared Vibrational Frequencies (cm^{-1}) of TCNX Anion Radicals and of Their Diruthenium Complexes^a

radical species	$\tilde{\nu}_{\text{C}\equiv\text{N}}$		$\tilde{\nu}_{\text{C}=\text{O}}$	$\tilde{\nu}_{\text{C}=\text{C}}$	
TCNE ^{•-}		2185 2140			1370
[L _n Ru ₂ (TCNE)](TCNE)	2210 (w) 2195 (w) 2160 (m) 2105 (m)	2185 (w, sh) ^b 2140 (w) ^b	2070 (s) 2050 (s) 2020 (m)		1505 (m) ^c
[L' _n Ru ₂ (TCNE)](TCNE)	2210 (w, sh) 2195 (w, sh) 2160 (m) 2100 (m)	2185 (m) ^b 2145 (w) ^b	2050 (s) 2030 (s) 2000 (s)		1505 (m) ^c
TCNQ ^{•-} ^d		2197 2166			1578, 1505, 1475, 1343
[L _n Ru ₂ (TCNQ)](BPh ₄)	2195 (m) 2145 (m) 2100 (w)		2060 (s) 2040 (s) 2008 (m)	1595 (s) 1505 (s) 1345 (w)	
[L _n Ru ₂ (TCNQ)](TCNQ)	2200 (m) 2152 (m) 2108 (w)	2180 (s) ^b 2152 (m) ^b	2060 (s) 2040 (s) 2008 (m)	1595 (s) 1505 (s) 1350 (w, sh)	1545 (w) ^b 1510 (w, sh) ^b 1360 (m) ^b
[L' _n Ru ₂ (TCNQ)](BPh ₄)	2190 (m) 2143 (m) 2098 (w)		2050 (s) 2030 (s) 1995 (m)	1600 (m) 1505 (m)	
[L' _n Ru ₂ (TCNQ)](TCNQ)	2195 (m, sh) 2150 (m) 2100 (m)	2180 (s) ^b 2150 (m) ^b	2050 (s) 2030 (s) 1995 (m)	1600 (m) 1505 (s) 1360 (m)	

^a Measurements in dichloromethane solution. ^b Assigned to external TCNX^{•-}. ^c Tentative assignment for coordinated TCNE^{•-} (see text). ^d From ref 17 (film).

complexes have been prepared, it is the TCNQ analogues which show the higher dissociative lability because of the lower basicity and poorer π acceptor capability of TCNQ^{0/•-}.^{3b,c} Evidently, the characteristic inertness of bonds formed between low-valent ruthenium and nitrogen coordination centers stabilizes the compounds described here.

The cyclic voltammograms of the TCNE salts also display four distinct, reversible one-electron waves, two of which correspond to those observed for TCNE itself (Table I). Because of the instability of the [L'_nRu₂(η^1 -TCNE)](TCNE) salts, it was not possible to effect the exchange of the external TCNE^{•-} for a tetraphenylborate anion; however, the assignments of the four waves to redox couples of coordinated and free TCNE^{•-} given in Table I follow naturally from the assignments made for the TCNQ analogues.

As discussed below, the EPR data confirm that the TCNX ligands in the cations [L'_nRu₂(η^1 -TCNX)]⁺ are bonded to one ruthenium atom through a nitrile N-atom and that the unpaired electron is localized on the TCNX ligand, i.e. the ligand coordinates as a TCNX^{•-} radical anion to the dicationic diruthenium(I) fragment 3. However, the potentials in Table I show that the η^1 -coordinated TCNX^{•-} ligands are more difficult to oxidize than the external, dissociated TCNX^{•-} species. This is to be expected for a ligand which functions predominantly as a σ donor and, moreover, suggests that there is comparatively little π back-donation from the dicationic, highly electrophilic diruthenium(I) fragment to the coordinated TCNX^{•-}, in contrast to what has been observed for the neutral complexes (TCNX)Mn(CO)₂(C₅R₅) and (TCNE)Cr(CO)₂(C₆R₆) with their strong $d(\text{metal})/\pi^*(\text{TCNE})$ orbital mixing.^{3b}

Since all the physical measurements described below were carried out in dichloromethane solution, we have examined the cyclic voltammogram of the complex [L'_nRu₂(η^1 -TCNQ)](TCNQ) in CH₂Cl₂/0.1 M Bu₄NClO₄. The result is virtually identical to that obtained in benzonitrile (Table I); the reversible oxidation and reduction waves of bound and external TCNQ^{•-} occur well-separated at +0.16 V (η^1 -TCNQ/ η^1 -TCNQ^{•-}), -0.22 V (TCNQ/TCNQ^{•-}), -0.62 V (η^1 -TCNQ^{•-}/ η^1 -TCNQ²⁻), and -0.80 V (TCNQ^{•-}/TCNQ²⁻) vs Fc/Fc⁺.

Infrared Vibrational Spectroscopy. Both the C \equiv N and C=C stretching bands of the TCNX ligands and the carbonyl bands of the organometallic fragment can give information on the

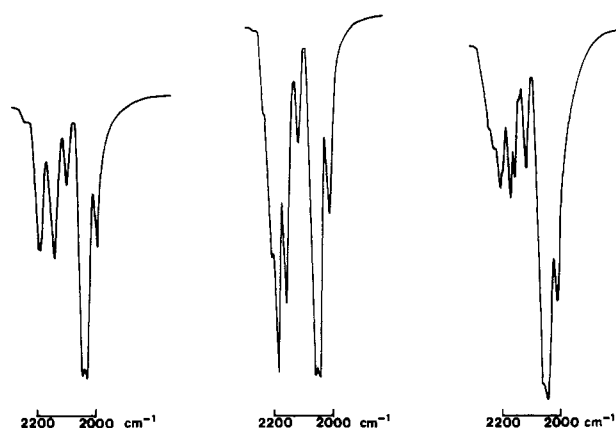


Figure 2. Infrared spectra of [L_nRu₂(TCNX)](A) in the C \equiv N and C=O vibrational stretching region: (left) TCNX = TCNQ, A = BPh₄; (middle) TCNX = TCNQ, A = TCNQ; (right) TCNX = TCNE, A = TCNE (all in dichloromethane solution).

symmetry and oxidation states of the components within the complexes.²⁻⁵ The frequencies from IR measurements in solution are summarized in Table II, while Figure 2 shows typical spectra for complexes with η^1 -coordinated and free TCNX^{•-} ligands.

When compared to IR data of "normal" complexes of the diruthenium(I) fragment 3,¹⁴ the number and frequencies of the metal carbonyl stretching bands exhibit very little change. This indicates that both the geometries within the framework (3) and the oxidation states of the metals are not affected by coordination of TCNX^{•-} anion radicals, in contrast to what has been observed with the Mn(CO)₂(C₅R₅) and Cr(CO)₂(C₆R₆) organometallic fragments.^{3b} This is in agreement with the electrochemical results mentioned above which also indicate relatively little mixing of Ru metal orbitals with the $\pi^*(\text{TCNX})$ orbital.

The number and intensity variations of nitrile stretching bands in the infrared spectrum are quite indicative of the coordination status of TCNX ligands.²⁻⁵ Whereas free, D_{2h}-symmetric species show a maximum of two such IR bands,⁹ the η^1 -coordinated TCNX molecules or ions should exhibit all four bands,^{2,3} the highest energy band being the weakest. The data from Table II confirm these expectations; for the η^1 -TCNE^{•-} and free TCNE^{•-}-containing complexes, a total of six C \equiv N stretching

bands are observed in solution of which two are straightforwardly assigned to free, dissociated TCNE⁻, the frequencies of the remaining four bands being typical of η^1 -coordinated TCNE⁻,^{2b,3a,b} In the case of the TCNQ⁻ complexes, the availability of stable tetraphenylborate salts allows an even easier assignment of bands to η^1 -TCNQ⁻ although only three bands can be clearly distinguished.

The major C=C and ring vibrations of TCNQ⁻ between 1300 and 1600 cm⁻¹^{17b} are also found in the BPh₄⁻ and TCNQ⁻ salts of [L^(I)_nRu₂(TCNQ)]^{+·} with relatively little frequency change (Table II). Less obvious are the results concerning the expected infrared-active C=C stretching vibration of η^1 -bonded TCNE⁻; this not very intense band should occur at lower energies than the value of 1569 cm⁻¹ recorded in Raman spectra of nonreduced TCNE;^{2c} a value of 1430 cm⁻¹ was given for the sodium salt,^{17b} and slightly lower numbers between 1380 and 1410 cm⁻¹ were reported for neutral complexes with η^1 -bonded TCNE⁻.^{2b,3a,b} Of the two new bands at 1325 and 1505 cm⁻¹ which appear on formation of [L^(I)_nRu₂(TCNE)](TCNE), we tentatively assign the latter as $\bar{\nu}(\text{C}=\text{C})$ because we assume an increase relative to free TCNE⁻ due to the positive charge and the small extent of π back-donation.

EPR/ENDOR Spectroscopy. In the absence of intramolecular spin coupling among TCNX⁻ ligands or between TCNX⁻ ligands and metal centers, the individual external and η^1 -coordinated TCNX⁻ ligands should be clearly identifiable by high-resolution EPR or ENDOR spectroscopy in solution. Whereas the spectroscopic properties of noncoordinated TCNX⁻ ions are well documented,¹⁶ there is only little previous EPR information on η^1 -coordinated TCNX⁻ species. Prior to the study of the pentacarbonyltungsten complex of η^1 -TCNE⁻,¹⁸ there had only been a report by Krusic and co-workers on unstable neutral carbonylmetal species;¹⁹ on the other hand, η^1 -TCNQ⁻ had never been studied before in detail by high-resolution EPR or ENDOR spectroscopy. This lack of information is not surprising because the lowered symmetry should give rise to four different ¹H- and four different ¹⁴N-coupling constants with 2⁴ × 3⁴ = 1296 theoretical lines; considering the typically small coupling constants of TCNQ⁻ species, this should lead to extensive overlapping of hyperfine lines. Additional complications through other coupling nuclei such as ³¹P (as in the case of the complexes [L^(I)_nRu₂(η^1 -TCNX)]^{+·}) and through the presence of free TCNX⁻ makes the EPR spectral interpretation of these materials even more complicated so that several measures had to be taken in order to arrive at a satisfactory analysis.

First, a Hückel MO/McLachlan perturbation calculation was performed on TCNQ⁻ where the η^1 -coordination was mimicked by a change in the Coulomb integral parameter at one nitrile nitrogen center.²⁰ All other parameters were used as introduced by Rieger and Fraenkel.¹⁶ The result of this perturbation procedure as illustrated in Figure 3 is quite remarkable. Not only the N π spin populations, $\rho_N(\pi)$, but also the CH π spin densities follow a pattern as calculated similarly for η^1 -TCNE⁻,¹⁸ that is, virtual C_{2v} symmetry is present because corresponding nuclei from the "remote" half of the molecule show an identical increase for $\rho_N(\pi)$ whereas the pertinent centers on the "coordinated side" of TCNQ⁻ experience a decrease of π spin population after increasing h_N of one nitrile group. Only $\rho_N(\pi)$ of the coordinated nitrile center shows a slight deviation from the virtual C_{2v} symmetry which persists despite the C_s symmetry imposed by the perturbation.

A second measure to reduce the anticipated complexity of EPR spectra was to use ENDOR spectroscopy, at least for the coupling

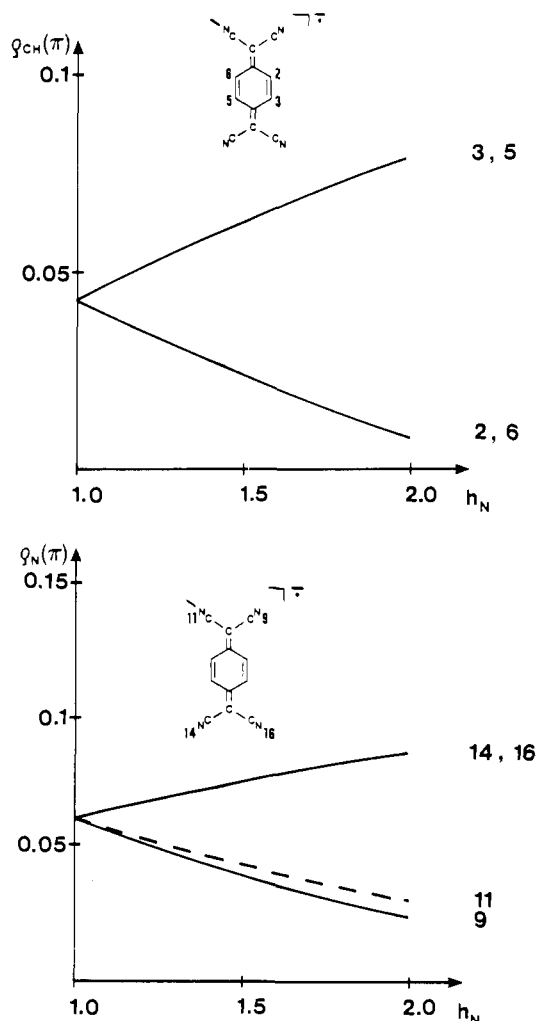


Figure 3. Variations of Hückel MO/McLachlan spin populations $\rho(\pi)$ for CH centers (top) and N atoms (bottom) of TCNQ⁻ upon perturbation ($1.0 < h_N < 2.0$) at one (N_{11}) of the four nitrogen centers. Other parameters: $h_N = 1.0$; $k_{\text{C}=\text{N}} = 2.0$.^{16a}

¹H nuclei in [L^(I)_nRu₂(TCNQ)](BPh₄). The ¹⁴N-coupling constants are too small to be determined within the frequency range above 5 MHz; however, a signal from a third type of nucleus, identified as ³¹P, could be detected. As Figure 4 demonstrates, the ¹H-ENDOR spectrum indeed agrees perfectly with the predictions from HMO perturbation theory; one set of hydrogen coupling constants (H_2, H_6) has become very small whereas the coupling constant of the other two protons H_3 and H_5 has increased by about the same amount. Only two ¹H-coupling constants are observed within the ENDOR line width, again in agreement with the HMO/McLachlan calculation results (Figure 3). Successful simulations of the EPR spectra (Figure 6) confirm that each ¹H-ENDOR coupling constant belongs to two protons. An ENDOR spectrum of the complex [L^(I)_nRu₂(TCNQ)](TCNQ) in solution (Figure 4) shows strong signals from free TCNQ⁻ (with an "average" coupling constant) and weak features of η^1 -coordinated TCNQ⁻; the dispersion of the intensity on to very many EPR lines is probably responsible for the comparatively weak ENDOR lines of η^1 -TCNQ⁻.

The rather large total width, particularly of the EPR spectra of the TCNE complexes, prompted us to analyze these spectra on the basis of similar HMO perturbation calculations and previous results for η^1 -TCNE⁻ complexes.¹⁸ While the absence of ¹H-coupling constants and the larger π spin populations in this smaller π system were expected to facilitate the spectral analysis, the presence of free TCNE⁻ in the complexes [L^(I)_nRu₂(TCNE)](TCNE) proved to be a complicating factor. Taking advantage of the electrochemical data (Table I), we were able, however, to

(17) (a) Hinkel, J. J.; Devlin, J. P. *J. Chem. Phys.* **1973**, *58*, 4750. (b) Khatkale, M. S.; Devlin, J. P. *J. Chem. Phys.* **1979**, *70*, 1851.

(18) Roth, T.; Kaim, W. *Inorg. Chem.* **1992**, *31*, 1930.

(19) Krusic, P. J.; Stoklasa, H.; Manzer, L. E.; Meakin, P. *J. Am. Chem. Soc.* **1975**, *97*, 667.

(20) Kaim, W. *Coord. Chem. Rev.* **1987**, *76*, 187.

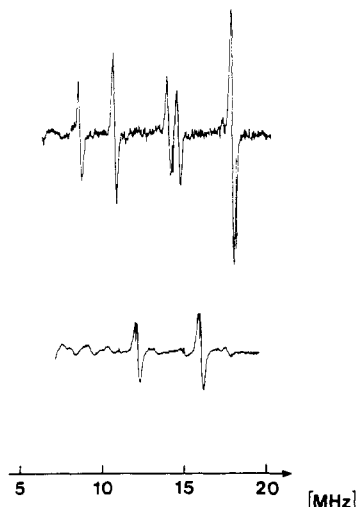


Figure 4. ENDOR spectra of $[L'_nRu_2(TCNQ)]^{+\bullet}$ (A) with $A = BPh_4^-$ (top) and $A = TCNQ^{\bullet-}$ (bottom) at 263 K in dichloromethane solution. Proton hyperfine lines are centered around the "free" frequency of $\nu(^1H) = 14.15$ MHz (ENDOR resonance condition $\nu = |\nu_X \pm a/2|$); the signal at 8.3 MHz is assigned as a ^{31}P ENDOR line ($\nu_P = 5.45$ MHz, $a(^{31}P) = 5.7$ MHz; 1 mT = 28 MHz).

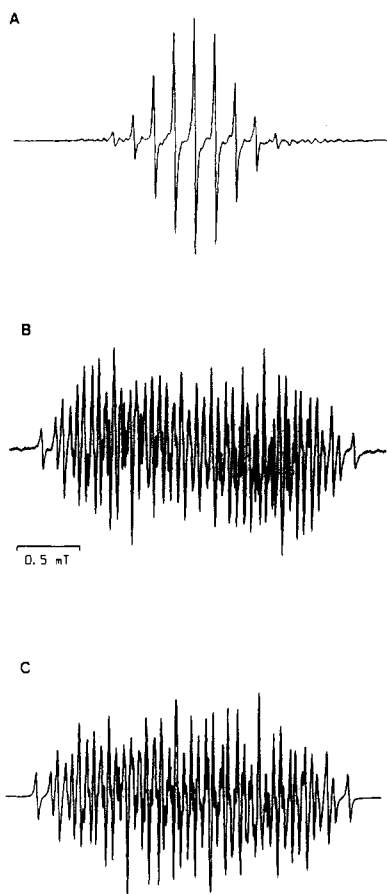
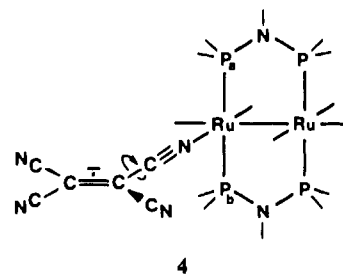


Figure 5. EPR spectra of $[L'_nRu_2(TCNE)](TCNE)$ before (top, A) and after oxidation of external $TCNE^{\bullet-}$ with ferrocenium ion (middle, B) at 300 K in dichloromethane and computer simulation (bottom, C) of the spectrum B of the complex cation using the parameters from Table II and a line width of 0.028 mT.

selectively oxidize free $TCNE^{\bullet-}$ using the ferrocenium ion to neutral, diamagnetic TCNE and to thus observe the undisturbed EPR spectra of $[L'_nRu_2(TCNE)]^{+\bullet}$ (Figure 5). The rather large difference in spectral width and hyperfine structure between the methoxy (L) and isopropoxy derivatives (L') led us to include rather large ^{31}P hyperfine coupling constants from two P nuclei into the analysis; the best results were obtained with a slightly

different ^{31}P coupling constant for each of the two P atoms (Figure 5 and Table III).

The molecular basis for the necessity to include two slightly different phosphorus centers into the EPR hyperfine coupling pattern is the assumed, slightly skewed conformation (4) in which



the π system of the coordinated η^1 -TCNE $^{\bullet-}$ ligand can interact hyperconjugatively (π^*/σ^*) with two approximately parallel Ru-P bonds. Previous studies on anion-radical ligands coordinated to species with adjacent M-P bonds have shown that rather large ^{31}P hyperfine coupling constants occur in those cases where the ligand π^* system and the metal-to-phosphorus σ bond are situated essentially parallel to each other.^{20,21}

As for $(CO)_5W(\eta^1-TCNE^{\bullet-})$ with $a(^{14}N) = 0.134$ (1 N), 0.166 (2 N), and 0.246 mT (1 N),¹⁸ the ^{14}N -coupling constants of η^1 -coordinated TCNE $^{\bullet-}$ in the TCNE salts display a distinct pattern; there is one small value, two indistinguishable intermediate coupling constants, and one large splitting parameter. The latter is attributed to the nitrile nitrogen center bonded to the metal because the coordination of a metal is known to increase the coupling constant of a nitrogen center, quite independently of the spin density.^{20,22} Of the remaining coupling constants, the small value for one ^{14}N nucleus is assigned to the free nitrile group which is geminal to the metal-coordinated nitrile site of TCNE $^{\bullet-}$ (corresponding to N_9 of η^1 -TCNQ $^{\bullet-}$; Figure 3), whereas the splitting constant for the two spectroscopically equivalent nuclei is assigned to the two "remote" nitrogen centers of TCNE $^{\bullet-}$, corresponding to N_{14} and N_{16} of η^1 -TCNQ $^{\bullet-}$ (Figure 3). Such an assignment is in agreement with calculated spin distributions for η^1 -TCNE $^{\bullet-}$ ¹⁸ and η^1 -TCNQ $^{\bullet-}$ (Figure 4), considering the special effect of metal binding to the coordinated nitrile group. A successful EPR simulation was thus finally possible even for the η^1 -TCNQ $^{\bullet-}$ complexes (Figure S1 (supplementary material) and Table III) which should—theoretically—have 10 different coupling constants (4 1H , 4 ^{14}N , 2 ^{31}P) with a total of 5184 lines.

The low symmetry of the complexes and the relatively poor signal-to-noise ratio in the well-resolved EPR spectra did not allow us to detect ^{13}C or $^{99,101}Ru$ isotope coupling.²³ Metal hyperfine coupling should be rather small in any case, considering the very minute extent of ligand/metal orbital mixing and the small absolute π spin population at the coordinating nitrile nitrogen center (cf. Figure 3).^{20,22}

In addition to the hyperfine splitting, the g factor of radicals can also give some information regarding electronic structure.²⁰ When compared to free TCNX $^{\bullet-}$ ions, all coordinated species described in this study have smaller g factors, generally a little lower than the free electron value of 2.0023. According to established theory,^{20,24} this result points to a situation in which higher excited states are rather close lying and in which admixture of these to the doublet ground state can occur via spin-orbit coupling. In the present case, such excitations could involve σ^* orbitals between the two ruthenium atoms or between ruthenium

- (21) (a) Creber, K. A. M.; Wan, J. K. S. *Can. J. Chem.* **1983**, *61*, 1017. (b) Kaim, W. *J. Organomet. Chem.* **1984**, *262*, 171. (c) Alberti, A.; Camaggi, C. M. *J. Organomet. Chem.* **1979**, *181*, 355.
 (22) Kaim, W.; Kohlmann, S. *Inorg. Chem.* **1986**, *25*, 3442.
 (23) Kaim, W.; Ernst, S.; Kasack, V. *J. Am. Chem. Soc.* **1990**, *112*, 173.
 (24) Fischer, H. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, p 452.

Table III. EPR/ENDOR Parameters of TCNX Anion Radicals and of Their Diruthenium Complexes^a

radical species	<i>g</i>	<i>a</i> (¹⁴ N)	<i>a</i> (³¹ P)	<i>a</i> (¹ H) ^b
TCNE ⁻	2.00273	0.157 (4 N)		
[L' _n Ru ₂ (TCNE)](PF ₆) ^c	2.00184	0.117 (1 N)	0.430 (1 P)	
		0.172 (2 N)	0.441 (1 P)	
		0.249 (1 N)		
[L' _n Ru ₂ (TCNE)](PF ₆) ^c	2.00199	0.117 (1 N)	0.523 (1 P)	
		0.172 (2 N)	0.536 (1 P)	
		0.251 (1 N)		
[L' _n Ru ₂ (TCNE)](TCNE)		overlapping spectra of TCNE ⁻ and [L' _n Ru ₂ (TCNE)] ⁺⁺		
TCNQ ⁻	2.00265	0.099 (4 N)		0.141 (4 H)
[L' _n Ru ₂ (TCNQ)](BPh ₄)	2.00220	0.054 (1 N)	0.189 (1 P)	0.022 (2 H)
		0.117 (1 N)	0.205 (1 P)	0.260 (2 H)
		0.133 (2 N)		
[L' _n Ru ₂ (TCNQ)](BPh ₄)	2.00222	0.055 (1 N)	0.198 (1 P)	0.018 (2 H)
		0.123 (1 N)	0.203 (1 P)	0.259 (2 H)
		0.131 (2 N)		
[L' _n Ru ₂ (TCNQ)](TCNQ)		overlapping spectra of TCNQ ⁻ and [L' _n Ru ₂ (TCNQ)] ⁺⁺		
[L' _n Ru ₂ (TCNQ)](TCNQ)		overlapping spectra of TCNQ ⁻ and [L' _n Ru ₂ (TCNQ)] ⁺⁺		

^a From measurements at room temperature in dichloromethane solutions. Coupling constants *a* in mT. ^b From ¹H-ENDOR measurements at 263 K. ^c Generated in situ from [L'_nRu₂(TCNE)](TCNE) via selective oxidation of external TCNE⁻ by ferrocenium hexafluorophosphate.

Table IV. Absorption Maxima (nm) of Diruthenium Complexes with TCNX Ligands in the Visible and Near-UV Regions^a

compd	λ _{max}
TCNE ^b	270
TCNE ⁻ - <i>b</i>	428 ^{b,c}
[L' _n Ru ₂ (TCNE)](TCNE)	428 ^c + long-wavelength shoulder
[L' _n Ru ₂ (TCNE)] ⁺⁺ ^d	309, 483
[L' _n Ru ₂ (TCNE)] ⁺⁺ ^e	310 (475 sh)
[L' _n Ru ₂ (TCNE)] ²⁺ ^f	402, 530 (MLCT)
TCNQ	399
TCNQ ⁻ ^g	420, 680, 743, 761, 842 (ε 43 300)
[L' _n Ru ₂ (TCNQ)](BPh ₄)	395 sh, 411, 424, 440 sh, 718, 799
[L' _n Ru ₂ (TCNQ)] ²⁺ ^f	415, 520 sh (MLCT)
[L' _n Ru ₂ (TCNQ)](BPh ₄)	397, 410, 422, 440 sh, 604 sh, 722 sh, 801 (ε 10 000)
[L' _n Ru ₂ (TCNQ)](TCNQ)	404, 422, 670 sh, 685 sh, 730 sh, 747, 765, 801 sh, 848 (ε 51 000) ⁱ
[L' _n Ru ₂ (TCNQ)] ²⁺ ^f	427, 600 sh (MLCT)
[L' _n Ru ₂ (TCNQ)] ⁰ ^h	480

^a In dichloromethane solution; molar extinction coefficients ε in M⁻¹ cm⁻¹. ^b See ref 7c. ^c Maximum of highly structured band. ^d From spectra subtraction: [L'_nRu₂(TCNE)](TCNE) - (TCNE⁻). ^e From partial oxidation of external TCNE⁻ by ferrocenium ion. ^f Obtained following complete oxidation of external and coordinated TCNX⁻ with AgPF₆. ^g Reference 25. ^h Generated via reduction with Bu₄NBH₄. ⁱ Bands assigned exclusively to free TCNQ⁻ are italicized.

and phosphorus centers as suggested by ³¹P coupling; in related cases, the anion-radical complexes of phosphine or phosphite organometallic fragments were also observed to exhibit decreased isotropic *g* factors.^{21a,b} Results from UV/vis/near-IR absorption spectroscopy will have to be correlated with this interpretation.

UV/Vis/Near-IR Absorption Spectroscopy. Both the TCNE⁻ and the TCNQ⁻ anion radicals exhibit very distinct, partially structured absorption spectra in the visible region (Table IV).^{7c,25} While these features are certainly present in the solution spectra of those complexes with external, dissociated TCNX⁻ counteranions, we have tried to obtain absorption data for species containing only η¹-coordinated TCNX⁻ and for some oxidized and reduced forms.

The most straightforward results come from studies of the tetraphenylborate salts [(L'_nRu₂(TCNQ)](BPh₄), the spectrum of one example being shown in Figure 6. The spectrum is clearly similar to that of free TCNQ⁻; as expected, the bands are less well structured and less intense. There is also a general shift for both band systems at about 700 and 420 nm to slightly higher energy upon coordination.

The complexes with external TCNX⁻ counterions exhibit overlapping spectra of free and coordinated anion radicals. In

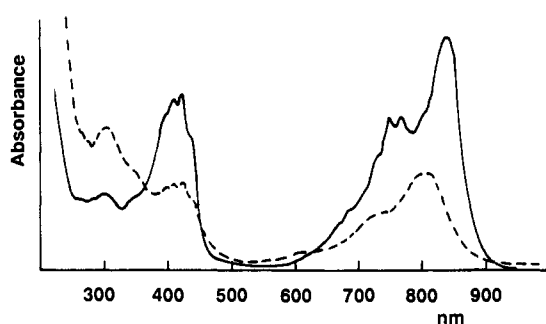


Figure 6. UV/vis/near-IR absorption spectrum of [L'_nRu₂(TCNQ)]⁺⁺ (A), A = BPh₄⁻ (---) and TCNQ⁻ (—) in dichloromethane solution (absorbance scale different for each spectrum).

the case of the [L'_nRu₂(TCNE)]⁺⁺ systems, both the chemical oxidation of external TCNE⁻ by the ferrocenium ion and subtraction of the structured TCNE⁻ spectrum from that of the dissociated complex [L'_nRu₂(TCNE)]⁺⁺(TCNE)⁻ revealed absorption maxima at 480 and 310 nm.

Oxidation of the paramagnetic complex cations to dications containing neutral TCNX ligands has been achieved with AgPF₆ in dichloromethane solution. There is a slight shift of the typical absorption at 399 nm for "free" TCNQ to about 420 nm for the neutral η¹-bound ligand, in agreement with the stabilization of the LUMO in the complex as evident from cyclic voltammetry (Table I). Moreover, the spectra of the dications show relatively weak long-wavelength features between 400 and 600 nm, which are interpreted as metal-to-ligand charge-transfer (MLCT) bands: d(Ru) → π*(TCNX). The relatively low intensities of these bands confirm the weak π interaction of the organometallic fragment and the TCNX ligands; the comparatively^{3b} high energies of these transitions point to strongly stabilized occupied metal d orbitals. Reduction of [L'_nRu₂(TCNQ)](BPh₄) to the dissociatively labile neutral complex resulted in the appearance of one low-intensity absorption at 480 nm in the visible region.

Summary. The compounds {Ru₂(CO)₅[μ-(RO)₂PN(Et)P(OR)₂]₂(η¹-TCNX)}⁺⁺(A)⁻, A⁻ = TCNX⁻ or BPh₄⁻, are clearly dissociated in dichloromethane solution into radical-cationic complexes containing η¹-coordinated TCNX⁻ radical-anions and counteranions which can be "innocent", such as BPh₄⁻, or paramagnetic and redox-active, such as "free" TCNX⁻. With the help of Hückel MO/McLachlan perturbation calculations and high-resolution EPR/ENDOR spectroscopy, the response of TCNE⁻ and, for the first time, TCNQ⁻ anion radicals toward η¹-coordination by an electrophilic metal center could be established. In spite of the rather weak metal/TCNX π interaction as evident from detailed electrochemical and IR-, EPR/ENDOR, and UV/vis-spectroscopic studies, the complex radical

cations are relatively inert toward dissociation of the TCNX⁻ bound in the first coordination sphere. Therefore, these "metal-modified" TCNX⁻ species may be suitable as *cationic* functional components in molecular solids with special magnetic, optical, or conductive properties.

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Supplementary Material Available: An EPR spectrum of [L_nRu₂(TCNQ)]²⁺(BPh₄)⁻ with computer simulation (Figure S1), UV/vis absorption spectra of [L_nRu₂(TCNE)](TCNE) and of TCNE⁻ (Figure S2), and UV/vis absorption spectra of TCNQ and of [L_nRu₂(TCNQ)]²⁺ (Figure S3) (4 pages). Ordering information is given on any current masthead page.