ORGANOMETALLICS

Reactions of 7,7,8,8-Tetracyanoquinodimethane with Poly-ynyl Ruthenium and Iron Complexes

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Supporting Information

ABSTRACT: The reaction of tetracyanoquinodimethane (TCNQ) with Ru(C=CC=CH)(dppe)Cp* (5) at the outer (from Ru) C=C triple bond gives η^1 -(butadienyl)ethynyl Ru{C=CC[CH=C(CN)_2]=C_6H_4=C-(CN)_2}(dppe)Cp (8), which reacts with a second equivalent of diynyl-Ru complex to give {Ru(dppe)Cp*}{C=CC[=C_6H_4=C(CN)_2]CH=CHC[=C(CN)_2]C=C}{Ru(dppe)Cp*} (9). The Ph-substituted complexes M{C=CC=CPh}(dppe)Cp* (M = Fe 6-Fe, Ru 6-Ru) and Ru{(C=C)_3Ph}(PPh_3)_2Cp (7) react with TCNQ to give the η^1 -(butadienyl)ethynyls M{C=CC[CPh=C(CN)_2]=C_6H_4=C(CN)_2}-(dppe)Cp (10-Fe, 10-Ru) and Ru{C=CC[C(C=CPh)=C(CN)_2]=C_6H_4=C(CN)_2}-(dppe)Cp (11), respectively. Single-crystal X-ray diffraction molecular structure determinations for 8–11 have been carried out. In the Fe series, we suggest that the initial step of the mechanism involves electron transfer to form the [TCNQ]^{-•} salt of the diynyl-iron cation,



followed by C–C bond formation to give a zwitterionic intermediate. Isolated products can be rationalized by further reaction involving [2 + 2]-cycloaddition of one of the C=C(CN)₂ groups of TCNQ to a C≡C triple bond of the metal poly-ynyl complex and a subsequent ring-opening reaction of the resulting (unobserved) cyclobutenyl intermediate. On the basis of X-ray diffraction data, redox potential determinations, and ⁵⁷Fe Mössbauer and UV–vis spectroscopies, the electronic structures of the new compounds contain significant contributions from polarized mesomers involving charge transfer from the electron-rich metal–ligand fragment to the cyanocarbon ligand via the conjugated unsaturated carbon linker.

INTRODUCTION

There is considerable current interest in the synthesis and properties of molecules containing an electron-rich center linked by a bridge containing a conjugated π -system to an electron-accepting fragment (D- π -A systems). These compounds are strongly polarized and consequently, among other features, show efficient nonlinear optical properties.¹⁻⁴ Popular electron-accepting molecules are the cyano-alkenes, for example but not limited to tetracyanoethene [(NC)₂C=C(CN)₂, TCNE] and tetracyanoquinodimethane [(NC)₂C=C(CN)₂, TCNE] and tetracyanoquinodimethane [(NC)₂C=C₆H₄= C(CN)₂, TCNQ]. The strong electron-accepting properties of these molecules have been known for more than half a century, with the formation of a large range of charge-transfer (CT) adducts, and their opto-electronic, magnetic, and conduction properties have resulted in applications as p-dopants for solar cells and light-emitting diodes.

Studies of their addition to donor-substituted alkynes, particularly *N*,*N*-dialkylanilino derivatives, are of more recent origin.⁵ Reactions between the cyano-alkenes and these donor-substituted alkynes commonly proceed via [2 + 2]-cyclo-addition reactions to give cyclobutenes, which may react further

by ring-opening (retro-electrocyclic reactions) to give substituted butadienes. Similar chemistry of alkynyl-metal complexes was first described in 1972 (for TCNQ) and 1979 (for TCNE), with completely regioselective [2 + 2]-cycloaddition of TCNQ being found. The butadienes formed by subsequent ring-opening reactions contain nonplanar chromophores that have unusual redox and opto-electronic properties.⁶

Studies of homo- and hetero-organobimetallics with various carbon bridges have also been the subject of intense efforts over recent years. These multifunctional molecular arrays have been extensively investigated in order to establish variations in their electronic, magnetic, and optical properties as a function of differing metal oxidation states.^{7–11} More recently, hybrid systems containing both metallic and organic electrophores have shown properties that, like the organic D- π -A systems mentioned above, may make these materials suitable for incorporation into components for molecular electronic and NLO assemblies.^{12,13}

Received: July 19, 2012 Published: September 10, 2012

Reactions of electron-deficient alkenes, such as TCNE, with transition metal complexes have attracted interest for many years, those with alkynyl and poly-ynyl derivatives affording an extensive chemistry that again originates from the donor–acceptor interactions.^{14,15} As shown in Scheme 1, initial

Scheme 1. Reactions of TCNE with Alkynyl-Transition Metal Complexes a



^aKey: (i) [2 + 2]-cycloaddition; (ii) R = H: CN displacement (-HCN).

formation of a radical anion salt of the oxidized alkynyl-metal complex A (CT complex) is followed by C–C bond formation to give **B**, which undergoes intramolecular [2 + 2]-cycloaddition to give cyclobutene C and subsequent ring-opening reactions affording D and E, the latter being formed by displacement of a 2-e donor ligand from the metal center. Further studies have revealed that highly nucleophilic ethynylmetal complexes can also react by substitution of a CN group of TCNE, with concomitant elimination of HCN, to give the ethynyl-tricyanovinyl complexes $\{ML_n\}C \equiv CC(CN) = C$ - $(CN)_2$, F. These are further examples of D- π -A systems, in which an organometallic donor is linked via a σ -ethyndiyl (C C) connector to an organic acceptor ligand.¹⁶ Unusual electronic properties of $Ru\{C \equiv CC(CN) = C(CN)_2\}(dppe)$ -Cp*, which can be obtained in nearly quantitative yield from $Ru(C \equiv CH)(dppe)Cp^*$ and TCNE, are evidenced by its intense purple color arising from an intramolecular CT band at ca. 557 nm in CH₂Cl₂, which shows pronounced solvatochromism.¹⁶

The competition between (i) [2 + 2]-cycloaddition and (ii) CN-displacement, as depicted in Scheme 1, depends on the nature of the R group (H vs Ph) and also on the electronic and steric properties of the alkynyl-metal fragment. In this case, the use of more sterically hindered alkynyl-metal derivatives favors route (ii) and allows access to hybrid molecules containing an electron-rich MLn fragment linked to a strongly electrophilic organic acceptor by the C \equiv C moiety. In these complexes, this arrangement favors the π -d interaction between the two electrophores. The resulting tricyanovinylethynyl (tricyanobutenynyl) complexes are examples of polarized D- π -A systems.

Although the chemistry with TCNE is well-established,¹⁵ related studies of TCNQ are still somewhat limited in scope. The deep red-purple complexes obtained from *trans*-Pt(C \equiv CR)₂(PR'₃)₂ (R = H, Me, Et; R' = Me, Et) and TCNQ were initially considered to be the CT adducts,¹⁷ but were later shown by an X-ray study to be the butadienyl-platinum(II) derivatives, *trans*-Pt(C \equiv CR){C[=C₆H₄=C(CN)₂]CR=C-(CN)₂}(PR'₃)₂, formed by [2 + 2]-cycloaddition of TCNQ to one C \equiv C triple bond, followed by ring-opening of the resulting cyclobutenyls.¹⁸ Similar chemistry was described

In a more detailed study, we have recently described reactions of TCNQ with alkynyl-iron or -ruthenium complexes (Scheme 2).²¹ These follow pathways similar to those found for





"Key: (i) [2 + 2]-cycloaddition; (ii) ring-opening; (iii) chelation by loss of a 2-e donor ligand; (iv) R = H: CN-displacement.

TCNE, although it has also been possible to isolate and structurally characterize examples of the radical ion pair G (formed by 1-e oxidation) and the zwitterionic intermediate H (assumed but not previously isolated during related studies with TCNE), as well as the spiro-cyclobutenyl I and the η^{1} - and η^3 -butadienyls (J and K, respectively). The synthesis and the characterization of the CN-substituted product L, exemplified by the new hybrid complex 1 (see Chart 1), from TCNQ and $Ru(C \equiv CH)(PPh_3)_2Cp$ (2), was also achieved. Compound 1 contains the electron-rich organometallic donor $Ru(PPh_3)_2Cp$ linked via a σ -ethyndiyl bridge to an organic acceptor fragment (a D- π -A system). The ultimate products again depend on the nature of the metal-ligand combinations, but extensive studies have shown that the reactions proceed by initial formation of a radical ion pair G or zwitterion H (the charge transfer is driven by accommodation of electronic charge on the dicyanomethylene group), followed by regiospecific formation of a cyclobutenyl I, which may undergo ring-opening to afford a butadienyl complex J. In some cases, where an easily displaceable 2-e donor ligand is present, further reaction can occur to give a η^3 -butadienyl K.

Double addition of TCNE to anilinobuta-1,3-diynes affords octacyano[4]dendralenes,²² while addition of 4-Me₂NC₆H₄C \equiv CH to the TCNE adduct of $4\text{-Me}_2\text{NC}_6\text{H}_4\text{C}\equiv\text{CCN}$ gave a diaryl-tetracyanopentafulvene.²³ Extension of the reactions of TCNE to poly-ynyl-metal complexes has shown that steric protection of the C=C triple bond adjacent to the metal center by the associated phosphine ligands usually results in cycloaddition of TCNE to the outer C≡C triple bond of diynyl and to the central triple bond of the triynyl, to give ethynylbutadienyl ligands (as in 4A, Scheme 3).^{24,25} In only one case so far, namely, Ru(C=CC=CFc)(dppe)Cp, has addition to each of the C \equiv C triple bonds been found, to give $Ru\{C[=C(CN)_2]C[=C(CN)_2]C\equiv CFc\}(dppe)Cp$ (3) and $Ru{C \equiv CC[=C(CN)_2]CFc=C(CN)_2}(dppe)Cp$ (4).^{25b} This behavior may result from the smaller size of Cp vs Cp*, but can also result from the presence of the weaker electrondonor Fc group, leading to competitive cycloaddition reactions

Article

Chart 1. Compounds Discussed in This Work



Scheme 3. Two Sites of Addition of TCNE to a Diynyl-Metal Complex



to each C=C triple bond. The ethynylbutadiene 4 shows a distinct structural distortion toward the zwitterionic (or vinylidene) formulation 4B shown in Scheme 3. Interestingly, an analogous situation occurs with the regioselective addition of TCNE to the C=C triple bonds of the diyne FcC=CC=CC=CC_6H_4NMe_2-4, which is directed by the strong anilino electron donor to its adjacent C=C triple bond. Protonation (HBF₄) of the NMe₂ group reduces its donor power sufficiently so that the Fc donor could activate the C=C triple bond adjacent to this group.^{12b}

With the dual intent of gaining additional insight into the reactivity of TCNQ with alkynyl-metal complexes and access to further examples of hybrid donor-acceptor compounds, we have now reacted some poly-ynyl-metal derivatives with TCNQ. This paper reports the rich chemistry found in reactions between this cyanocarbon and the group 8 derivatives $\operatorname{Ru}(C \equiv CC \equiv CH)(\operatorname{dppe})\operatorname{Cp}^*(5)$ and $M\{(C \equiv C)_{2+n}\operatorname{Ph}\}(\operatorname{PP})$ - $\operatorname{Cp}'[n = 0, M = \operatorname{Fe}, \operatorname{Ru}, (\operatorname{PP})\operatorname{Cp}' = (\operatorname{dppe})\operatorname{Cp}^*(6\operatorname{-Fe} \text{ and } 6\operatorname{-Ru}); n = 1, M(\operatorname{PP})\operatorname{Cp}' = \operatorname{Ru}(\operatorname{PPh}_3)_2\operatorname{Cp}(7)]$, from which we have prepared compounds 8-11 (Chart 1). Interestingly, compound 9 resulted from the unprecedented addition of two metal fragments to a single cyanocarbon molecule.

RESULTS

1. Preparation of the New Complexes. The reactions of TCNQ with **5**, **6-Fe**, **6-Ru**, and 7 are summarized in Schemes 4– and 5. The molecular structures of five complexes have been





Scheme 5. Reactions of TCNQ with $M\{(C \equiv C)_{2+n}Ph\}(PP)Cp' [n = 0, (PP)Cp' = (dppe)Cp*, M = Fe 6-Fe, Ru 6-Ru; n = 1, M(PP)Cp' = Ru(PPh_3)_2Cp 7]$



determined by single-crystal X-ray diffraction studies (Figures 1–4 and Table 1) and confirmed by elemental microanalyses and from their spectroscopic properties. In the case of the iron compound **10-Fe**, the nature of the iron–carbon bonding has been investigated by Mössbauer spectroscopy of a powdered sample. In addition, the redox properties and the UV–vis spectroscopy of **8**, **9**, **10-Fe**, **10-Ru**, and **11** were determined in solution.

i. Reaction of TCNQ with $Ru(C \equiv CC \equiv CH)(dppe)Cp^*$ (5). The two complexes 8 and 9 have been obtained from reactions between TCNQ and this diynyl-ruthenium complex (Scheme 4). If the reaction is carried out in THF with an excess of TCNQ, an instantaneous color change from yellow to dark green occurs, and subsequent purification of the product by preparative TLC affords a low yield of $Ru\{C \equiv CC[=C_6H_4=$ $C(CN)_2]CH = C(CN)_2\}(dppe)Cp^*$ (8), which is obtained as a dark green solid. The composition was confirmed by a highresolution ES-MS of M⁺. The IR spectrum contains $\nu(CN)$ (2193), $\nu(C \equiv C)$ (1940), and $\nu(C = C)$ bands (1586 cm⁻¹). In the ¹H NMR spectrum, Cp* (δ_H 1.38), CH₂ (1.94, 2.57), and



Figure 1. Plot of molecule 1 of $Ru\{C \equiv CC[=C_6H_4 = C(CN)_2]-CH = C(CN)_2\}(dppe)Cp* (8)$. Molecules 2–4 are similar. Hydrogen atoms have been omitted for clarity.



Figure 2. Plot of a molecule of $\{Cp^*(dppe)Ru\}\{C\equiv CC[=C_6H_4=C(CN)_2]CH=CHC[=C(CN)_2]C\equiv C\}\{Ru(dppe)Cp^*\}$ (9). Hydrogen atoms have been omitted for clarity.

aromatic (7.01–7.42) resonances are accompanied by a singlet at $\delta_{\rm H}$ 6.72 assigned to the CH=C(CN)₂ proton. In the ¹³C NMR spectrum, resonances occur at $\delta_{\rm C}$ 9.79, 96.61 (Cp*), 29.42–30.30 (CH₂), 124.75–138.22 (Ph + C₆H₄), and 218.70 (Ru–C, t), together with four CN signals between $\delta_{\rm C}$ 111.73 and 120.89. In addition, resonances at $\delta_{\rm C}$ 86.13, 145.01, 152.70, and 155.26 arise from the cyanocarbon skeleton.

The molecular structure of **8** was determined from a singlecrystal X-ray diffraction study, and a plot of the molecule is given in Figure 1. Selected structural data are presented in Table 1. The structure is that expected from ring-opening of the [2 + 2]-cycloadduct of one of the $=C(CN)_2$ double bonds with the outer $C \equiv C$ triple bond of the precursor diynyl complex. Thus, the Ru center is attached to the remaining $C \equiv$ C triple bond [Ru-C(11) 1.939(12), C(11)-C(12) 1.207(18) Å; values for molecule 1 cited], which in turn is a substituent on the dienyl system C(131)=C(13)-C(14)=C(15). As found both with similar products from reactions of TCNE and for organic adducts of cyanocarbons with donor-substituted alkynes,^{Sb} there is a marked dihedral [50.6(6)°] between the



Figure 3. Plots of single molecules of $M{C \equiv CC[=C_6H_4=C(CN)_2]CPh=C(CN)_2}(dppe)Cp^* [M = Fe 10-Fe (left) and M = Ru 10-Ru (right)].$ Hydrogen atoms have been omitted for clarity.



Figure 4. Plot of a molecule of $Ru{C \equiv CC[=C_6H_4=C(CN)_2]C[=C(CN)_2]C \equiv C(CN)_2]C \equiv C(Ph_3)_2Cp$ (11). Hydrogen atoms have been omitted for clarity.

two C=C double bonds. The structure determination reveals that the C₆ quinoid group is attached to C(13), i.e., nearer to the electron-rich metal center, with the =C(CN)₂ group being attached to C(14). This mode of addition was previously found in reactions of TCNQ with Ni(C=CR)(PPh₃)Cp,¹⁹ Ru(C= CR)(dppe)Cp* (R = H, Ph),²¹ and Ru{C=CC=CC= C[CCo₃(μ -dppm)(CO)₇]}(dppe)Cp*.²⁰ In all of these reactions, cycloaddition of TCNQ is stereospecific, the =C(CN)₂ group residing further from the metal center; no evidence was found for the formation of any isomeric product resulting from the alternative mode of addition.

When the reaction between TCNQ and Ru(C \equiv CC \equiv CH)(dppe)Cp* was carried out in benzene, a different product was obtained in low yield, namely, dark brown {Cp*(dppe)-Ru}{ μ -C \equiv CC[=C₆H₄=C(CN)₂]CH=CHC[=C(CN)₂]-C \equiv C}{Ru(dppe)Cp*} (9). The dimeric formulation was confirmed by high-resolution ES-MS, and the two Ru(dppe)-Cp* groups could be distinguished in the NMR spectra. Thus, in the ¹H NMR spectrum, the two Cp* resonances are at $\delta_{\rm H}$

1.51 and 1.53; the two dppe CH₂ signals are found at $\delta_{\rm H}$ 1.99– 2.12 (4H) and 2.68, 2.82 (2 × 2H). In the ¹³C NMR spectrum, the two Cp* groups give Me resonances at $\delta_{\rm C}$ 10.28, 10.41 and ring C signals at $\delta_{\rm C}$ 95.56 and 96.62. There are also two broad Ru–C triplet resonances at $\delta_{\rm C}$ 191.89 and 210.57. Other signals include four CN signals between $\delta_{\rm C}$ 114.43 and 118.95, with two cyanocarbon skeleton resonances at $\delta_{\rm C}$ 77.10 and 121.17. Two ³¹P signals at $\delta_{\rm P}$ 80.7 and 81.8 arise from the two dppe ligands. The IR spectrum was similar to that of **8**, with ν (CN) (2186), two ν (C=C) (1983, 1947), and ν (C=C) (1579 cm⁻¹) bands.

Figure 2 is a plot of a molecule of 9; selected structural data are presented in Table 1. This shows that two Ru(dppe)Cp* groups at each end of a C₈ chain bear the $=C(CN)_2$ and =C₆H₄ $=C(CN)_2$ components of the TCNQ molecule attached to C(3) and C(6), respectively [C(6)–C(61) 1.398(5), C(3)– C(31) 1.425(5) Å]. The C(4)=C(5) fragment [1.339(5) Å] carries one H atom on each carbon, with angles C(3)–C(4)– C(5) and C(4)–C(5)–C(6) of 125.1(4)° and 121.6(4)°, respectively. The Ru atoms are attached to C(1) and C(8) of the two end C \equiv C triple bonds [Ru(1)–C(1) 1.952(4), Ru(2)–C(8) 1.943(4), C(1)–C(2) 1.233(5), C(7)–C(8) 1.227(5) Å].

The formation of 9 is notable in that the second addition occurs to the dienyl-bonded $C=C(CN)_2$ group of 8 rather than to the other $C = C(CN)_2$ moiety of the TCNQ. We note that the two components of the original TCNQ reactant are now separated by a -CH=CH- fragment, so that it is unlikely that **9** was formed by addition of TCNQ to an Ru- $(C \equiv C)_4$ -Ru precursor, which might have been formed by oxidative coupling of the diynyl complex.²⁶ Instead, we favor a route whereby a molecule of 8 reacts with a second molecule of the diynylruthenium complex, with a [2 + 2]-cycloaddition to the $C(14) = C(CN)_2$ fragment, followed by the usual ring-opening step (as shown in Scheme 4). Indeed, the reaction between 8 and a second equivalent of 5 afforded 9 in 56% yield. It is also likely that charge separation within the metal-cyanocarbon array, facilitated by both the electron-richness of the former and the electrophilic properties of the latter, and the steric influence of the diphosphine ligand play roles in the course of this reaction.

ii. Reaction of TCNQ with $M(C \equiv CC \equiv CPh)(dppe)Cp^*$ (M = Fe, 6-Fe; M = Ru, 6-Ru). A rapid color change from orange to dark purple (Fe) or from yellow to dark blue (Ru) followed

Table 1. Selected Bond Parameters for TCNQ Complexes

	8 (molecule 1)	9	10-Fe ^{<i>a</i>}	10-Ru	11
Bond Distances (Å)					
Ru–P(1)	2.294(4)	2.274(1); 2.290(1)	2.2186(8)	2.287(2)	2.3059(3)
Ru-P(2)	2.287(4)	2.277(1); 2.298(1)	2.2160(8)	2.292(2)	2.3100(3)
Ru–C(cp)	2.229-2.301(15)	2.232-2.285(4);	2.122-2.156(3)	2.230-2.281(6)	2.235-2.266(1)
		2.235 - 2.286(4)			
(av)	2.260	2.249;	2.141	2.259	2.249
		2.261			
Ru-C(1)	1.939(12)	1.952(4)	1.811(3)	1.943(6)	1.931(1)
C(1)-C(2)	1.21(2)	1.233(5)	1.251(4)	1.223(9)	1.248(2)
C(2) - C(3)	1.45(2)	1.388(5)	1.383(4)	1.370(9)	1.379(2)
C(3) - C(4)	1.45(2)	1.457(5)	1.494(4)	1.497(9)	1.497(2)
C(3)-C(31, 32)	1.42(2)	1.425(5)	1.423(4)	1.430(9)	1.412(2)
C(n) - C(41)			1.480(4) [C(4)]	1.480(10) [C(4)]	
C(4) - C(5)	1.35(2)	1.339(5)	1.359(4)	1.341(9)	1.416(2)
C(5)-C(6)		1.464(5)			1.208(2)
C(5)-C(51, 52)	1.47, 1.43(2)		1.433, 1.439(4)	1.452, 1.450(10)	
C(6) - C(61)		1.398(5)			1.429(2)
C(34)-C(340)			1.418(4)	1.410(10)	
C(340)-C(341, 342)			1.416, 1.426(4)	1.419, 1.400(10)	1.420, 1.422(2)
Bond Angles (deg)					
P(1)-Ru-P(2)	83.5(1)	85.10(4);	85.97(3)	82.69(6)	102.91(1)
		83.63(4)			
P(1)-Ru-C(1)	79.2(4)	85.7(1);	89.59(9)	84.5(2)	89.68(4)
		82.2(1)			
P(2)-Ru-C(1)	88.6(4)	82.6(1);	82.96(8)	89.8(2)	89.21(4)
		85.5(1);			
Ru-C(1)-C(2)	166.9(12)	176.0(4)	174.3(2)	172.3(5)	174.7(1)
C(1)-C(2)-C(3)	178.8(17)	173.1(4)	172.6(3)	169.0(6)	169.9(1)
C(2)-C(3)-C(4)	116.8(13)	119.7(2)	112.7(2)	113.2(6)	114.1(1)
C(2)-C(3)-C(31, 32)	120.2(13)	119.6(4)	125.3(3)	127.0(6)	125.7(1)
C(3)-C(4)-C(5)	126.8(14)	125.1(4)	120.4(2)	120.3(6)	120.0(1)
C(3)-C(4)-C(n)			116.4(2) [C(41)]	115.1(6) [C(41)]	120.4(1) [C(40)]
C(4) - C(5) - C(6)		121.6(4)			174.8(1)
C(5)-C(6)-C(61)		119.9(4)			175.3(2)
C(34)-C(340)-C(341, 342)			121.3, 118.4(3)	121.2, 121.3(7)	121.8, 120.7(1)
C(341)-C(340)-C(342)				117.4(7)	117.5(1)
C(4)-C(5)-C(51, 52)	123.4, 120.9(13)		121.8, 115.5(3)	120.5(6), 124.2(7)	
C(51)-C(5)-C(52)				115.3(6)	

^aFor Ru, read Fe. For 8: C(34) - C(37) 1.39(2), C(37) - C(38,39) 1.39, 1.42(2) Å; C(34) - C(37) - C(38,39) 124.6, $115.7(14)^{\circ}$. For 9: Ru(2) - C(8) 1.943(4), C(6) - C(7) 1.396(5), C(7) - C(8) 1.227(5), C(34) - C(340) 1.409(5) Å; C(5) - C(6) - C(7) 119.5(4), C(4) - C(3) - C(31) 120.7(3), C(6) - C(7) - C(8) 177.1(4), $C(7) - C(8) - Ru(2) 178.8(3)^{\circ}$. For 11: C(4) - C(40) 1.361(2), C(40) - C(41,42) 1.430, 1.431(2) Å; C(4) - C(40) - C(41,42) 122.9, 120.8(1), $C(41) - C(40) - C(42) 116.2(1)^{\circ}$.

the addition of TCNQ to solutions of $M(C \equiv CC \equiv CPh)$ -(dppe)Cp* (6, M = Fe, Ru) in THF at rt. Purification by preparative TLC afforded dark blue $M\{C \equiv CC[=C_6H_4 = C(CN)_2]CPh = C(CN)_2\}$ (dppe)Cp* (10-Fe, 10-Ru) in moderate yields (Scheme 5). In the IR spectrum, $\nu(CN)$, $\nu(C \equiv C)$, and $\nu(C = C)$ bands are found at 2223, 1914, and 1579 (Fe) or at 2194, 1946, and 1585 cm⁻¹ (Ru).

The ¹H, ¹³C, and ³¹P NMR spectra of **10** contain the expected resonances [values for the Fe (Ru) complexes given] for the Cp* [$\delta_{\rm H}$ 1.21 (1.53), $\delta_{\rm C}$ 9.52, 96.54 (10.24, 98.17)], dppe [$\delta_{\rm H}$ 1.76–2.42 (2.22), $\delta_{\rm C}$ 30.87 (30.01–30.62), $\delta_{\rm P}$ 94.3 (80.5 br)], and Ph + C₆H₄ [$\delta_{\rm H}$ 6.85–7.60 (6.96–7.50), $\delta_{\rm C}$ 127.86–136.97 (128.38–137.47)] groups. In addition, the ¹³C NMR spectrum contains four resonances between $\delta_{\rm C}$ 58.28 and 171.56 assigned to carbons of the butadienyl skeleton, four resonances (in two pairs) between 113.03 and 123.20, assigned

to CN groups, and a downfield triplet at δ 244.90 (217.10), arising from the M-bonded carbon.

The single-crystal X-ray diffraction molecular structure determinations of **10-Fe** and **10-Ru** (Figure 3; selected structural data are presented in Table 1) showed that the products are butadienyls, likely formed by ring-opening of the undetected cyclobutenyls formed by [2 + 2]-cycloaddition of one $=C(CN)_2$ moiety to the outer $C\equiv C$ triple bond, in a fashion similar to the formation of **8**. Cleavage of the TCNQ molecule into $=C_6H_4=C(CN)_2$ and =C(CN) fragments has occurred, the former being attached to C(3) [C(3)-C(31) 1.423(4) [1.430(9)] Å; values for **10-Fe** (**10-Ru**) given], and the $=C(CN)_2$ group is attached to C(4) [C(4)-C(5) 1.359(4) [1.341(9) Å], the resulting diene again being nonplanar $[73.0(3)^\circ, (73.6(2)^\circ)]$.

In **10**, the usual $M(dppe)Cp^*$ moieties are attached to C(1)[M-C(1) 1.811(3) [1.943(6)], C(1)-C(2) 1.251(4) [1.223(9) Å]; values for Fe [Ru]]. Of interest is the contraction of the M–C bond from the ca. 1.90 (2.00) Å expected for an M–C(sp) bond [cf. 1.894(3) in Fe(C=CPh)(dppe)Cp^{*,27} 2.015(2) Å in Ru(C=CH)(dppe)Cp^{*28}], supporting a contribution to the structure from the zwitterionic formulation (see structures **A**, **B** in Scheme 5), with the positive charge centered on the metal center, resulting in some multiple-bond character for the M–C(1) link. The localization of negative charge on the remote =C(CN)₂ group is also indicated by the elongation of the C–CN bonds, compared with the values found for the C–CN bonds in the C₆H₄=C(CN)₂ group. The M–C(1)–C(2)–C(3) arrays are nearly linear, with angles at C(1) and C(2) of 174.3(2)° [172.3(5)°] and 172.6(3)° [169.0(6)°], respectively.

iii. Reaction of TCNQ with $Ru\{(C \equiv C)_3 Ph\}(PPh_3)_2 Cp, 7$. Addition of TCNQ to a solution of the triynyl complex $Ru\{(C \equiv C)_3 Ph\}(PPh_3)_2 Cp(7)$ in dichloromethane resulted in an immediate change of color from yellow to dark blue, the complex $Ru\{C \equiv CC[=C_6H_4 = C(CN)_2]C[=C(CN)_2]C \equiv$ CPh}(PPh₃)₂Cp (11) (Scheme 5) being precipitated by addition of hexanes to the concentrated reaction mixture. The composition was confirmed by a high-resolution ES-MS on $[M + H]^+$. In the IR spectrum, $\nu(CN)$, $\nu(C \equiv C)$, and $\nu(C \equiv$ C) bands are found at 2198, 1956, and 1590 cm^{-1} , respectively. The usual signals are present in the ¹H and ³¹P NMR spectra [at $\delta_{\rm H}$ 4.64 (Cp), 7.01–7.52 (Ph + C₆H₄), $\delta_{\rm P}$ 48.0], while the ¹³C NMR spectrum has resonances at $\delta_{\rm C}$ 61.77 (C \equiv C), 88.86 (Cp), 127.98-136.80 (Ph + C₆H₄), and 217.99 (Ru-C, t), together with several other cyanocarbon skeleton signals between $\delta_{\rm C}$ 86.75 and 154.05 and two pairs of CN resonances between δ 112.90 and 123.55.

Figure 4 is a plot of a molecule of 11 (selected structural data are presented in Table 1), from which it can be seen that the = $C_6H_4 = C(CN)_2$ fragment is attached to C(3) [C(3)-C(31)]1.412(2) Å] and the $=C(CN)_2$ group to C(4) [C(4)-C(40) 1.361(2) Å], i.e., the central two carbons of the C_6 chain in the triynyl precursor. Consequently, it is the Ru(PPh₃)₂Cp and Ph groups that are attached to the $C \equiv C$ groups at the ends of the chain [Ru-C(1) 1.931(1), C(1)-C(2) 1.248(2), C(5)-C(6) 1.208(2), C(6)-C(61) 1.429(2) Å]. Some lengthening of the inner C \equiv C bond to 1.248(2) Å is notable and is consistent with a significant contribution from structure **11B** (Scheme 5). In general, this structure has features similar to those of 10-Ru already described. Notable here, however, is the bending of the C_6 chain. Angles at C(1), C(2), C(5), and C(6) range between $169.9(1)^{\circ}$ and $175.3(1)^{\circ}$ (as expected for slightly distorted C(sp) atoms), whereas those at C(3) and C(4) are 114.1(1)° and $120.0(1)^\circ$, respectively, typical of $C(sp^2)$ atoms. Angles at individual C(sp) [C(1,2,5,6)] and at C(sp²) atoms [C(3,4)]sum to 151.2° from linear in a cumulative sense, so that the C(6)-C(61) vector is inclined at 55.0(2)° to the C(1)-C(2)vector.

2. Investigation of the Iron–Carbon Bonding by Mössbauer Spectroscopy. ⁵⁷Fe Mössbauer spectroscopy is a very sensitive probe for identifying the oxidation state of the iron and the nature of the Fe–C bond.^{29,30} The zero-field ⁵⁷Fe Mössbauer spectrum of a microcrystalline sample of the complex 10-Fe was obtained at 80 K and least-squares fitted with Lorentzian line shapes.³¹ The spectrum displays a unique doublet (Figure 5), proving the purity and the thermal stability of the sample. The half-widths at half-height [$\Gamma = 0.209(4)$ mm s⁻¹] of the two components of the doublet are relatively large,



Figure 5. ⁵⁷Fe Mössbauer spectrum of 10-Fe at 80 K.

but not exceptional, for compounds containing the Fe(dppe)- Cp^* moiety.³²

However, the isomeric shift $[IS = 0.187(3) \text{ mm s}^{-1} \text{ vs Fe}]$ is particularly small for a neutral compound. This parameter reflects the electron density at the iron nucleus and decreases as charge is progressively removed from the metal atom or less and less stabilized by electrostatic interaction between cations and anions.³³ In the case of compound **10-Fe** the value compares well with data obtained for iron carbene, vinylidene, or allenylidene complexes, in which the positive charge is localized on the metal center.³⁴

The quadrupole splitting parameter $[QS = 1.367(6) \text{ mm s}^{-1}]$ also does not match with the alkynyl-iron(II) structure depicted for **10-Fe** as structure **A** in Scheme 5. Indeed, for such a structure the expected QS value is close to 2.0 ± 0.1 mm s^{-1.32,34,35} In this series, QS values ranging between 1.0 and 1.5 are characteristic of cationic metallacumulenylidene complexes with the general structure $[Cp^*(dppe)Fe{=}C(=C)_nR_2]]X$ and consistent with a major contribution from Lewis structure **B** (Scheme 5) to the electronic structure of **10-Fe**.³⁴

3. Redox Properties. The initial scans of the CVs of complexes **8**, **9**, **10-Fe**, **10-Ru**, and **11** were run from -1.5 to +1.5 V vs SCE. The redox potentials and, when the redox processes are reversible, the peak-to-peak separations (ΔE_p) are collected in Table 2, and the CV of **10-Ru** is shown in Figure 6 as a representative example. For the four mononuclear compounds **8**, **10-Fe**, **10-Ru**, and **11**, the CVs display a single oxidation wave ($E^{0/1+}$) corresponding to the formation of the

Table 2. Electrochemical Data for 8, 9, 10-Fe, 10-Ru, 11, and Selected Compounds^a

compd	$E^{2-/1-} (\Delta E_{\rm p})$	$E^{1-/0}~(\Delta E_{ m p})$	$E^{0/1+}$ ($\Delta E_{\rm p}$)	$E^{1+/2+}$ ($\Delta E_{\rm p}$)
6-Fe ^b			-0.02 (0.06)	
6-Ru ^b			0.44 ^c	
1	-1.40^{c}	-0.50 (0.05)	0.76 ^c	
8	-0.72	-0.34	0.44 ^c	
9	-0.85 (0.05)	-0.52 (0.05)	0.57 ^c	0.80 ^c
10-Fe	-0.82 (0.15)	-0.49 (0.15)	0.42 (0.07)	
10-Ru	-0.62 (0.05)	-0.41 (0.05)	0.67 ^c	
11	-0.45 (0.05)	-0.27(0.05)	0.79 ^b	
TCNQ	-0.35 (0.05)	0.20 (0.05)		

"Potentials in CH₂Cl₂ (0.1 M [n-Bu₄N][PF₆], 20 °C, platinum electrode, sweep rate 0.100 V s⁻¹) are given in V vs SCE; the ferrocene–ferrocenium couple (0.46 V vs SCE) was used as an internal calibrant for the potential measurements. ^bFrom ref 36. "Irreversible.





corresponding radical cations at the platinum electrode. In the case of complex 10-Fe, the process found for the ${\rm Fe^{II}/Fe^{III}}$ redox couple is chemically reversible, indicating that the radical cation $[10-Fe]^+$ is thermally stable at the electrode. In contrast, the reverse reduction wave cannot be detected for the ruthenium complexes, indicating that the oxidized species rapidly decompose at the electrode. In the particular case of the binuclear complex 9, two irreversible oxidation waves were observed corresponding to the sequential oxidation of the two metal centers. The two different ruthenium ethynyl moieties of 9 oxidize independently at 0.57 and 0.80 V, and both give rise to chemically reactive species. In the case of the ruthenium complexes, the 1-e oxidation products are labile and rapidly decompose; the signatures of the resulting materials are found in the CVs during the back reduction. Indeed, the CVs of the ruthenium complexes 8, 9, 10-Ru, and 11 display reduction waves of weak intensity at 0.14, 0.78, 0.18, and 0.39 V, respectively, at potentials distinct from those of the $0/1^+$ redox couples.

The CVs of 8, 9, 10-Fe, 10-Ru, and 11 also show also two reversible or quasi-reversible reduction waves in the reduction range ($E^{1-/0}$ and $E^{2-/1-}$ in Table 2). These redox events are centered on the TCNQ side of the complexes, and the redox potentials are significantly more negative than that of TCNQ, showing that a strong electronic interaction between the electron-donor metal centers and the electron-withdrawing organic ligands occurs through the bridge. Similarly, one can also note that the oxidation potentials of the iron and ruthenium centers are both located at more positive potentials than those of **6-Fe** and **6-Ru**, consistent with the zwitterionic formulations indicated by the structural results.³⁶

UV–Vis Spectroscopy. The UV–vis spectra of 10-Fe, 10-**Ru**, and 11, chosen as representative of this series, were investigated at 20 °C in CH_2Cl_2 , and the data are collected in Table 3 together with those obtained previously for 1 for purposes of comparison.²¹ The spectra of these deeply colored

Table 3. UV–Vis Absorption Data for 10-Fe, 10-Ru, 11, and the Related Complex 1 in CH₂Cl₂ at 298 K

cmpd	absorption λ/nm ($\varepsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)
1^a	260 (87.9), 332 (15.9), 488 (5.1), 748 (66.7), 814 (73.6)
10-Fe	265 (46.2), 367 (8.9), 520 (9.8), 830 (35.9)
10-Ru	256 (32,3), 296 (20.0), 468 (6.9), 725 (32.6), 782 (56.3)
11	^b 354 (18.4), 587 (13.9), 706 (29.6, 761 (40.9)

^{*a*}From ref 21. ^{*b*}Measurement started at 350 nm.

complexes are very similar. Besides intense absorptions below 300 nm, which are assignable to intraligand transitions involving the C₅ ring and the phosphine ligands, the electronic spectra of the neutral species exhibit two absorptions each of medium intensity between 300 and 600 nm. By comparison with the related iron and ruthenium complexes bearing σ -acetylides substituents, these bands are tentatively assigned to $d\pi(M) \rightarrow \pi^*(C \equiv C)$ metal-to-ligand charge transfer transitions.^{36,38b} Additional broad and very intense bands that are responsible for the intense colors of these complexes were also found on the low-energy side of the spectra and extend into the near-IR. These bands are characteristic of CT transitions, and in the case of complex 1, it has been shown that these bands are solvatochromic.²¹

DISCUSSION

Previous studies of the reactions of TCNQ with alkynyl-group 8 complexes have resulted in complexes that may reasonably be expected to be formed by reactions summarized in Scheme 2. The adduct 8 has been identified here as the initial product from the reaction between TCNQ and Ru(C=CC=CH)-(dppe)Cp*, but this complex is accompanied by the binuclear adduct 9. The latter is the product of addition of two ethynylruthenium groups to one TCNQ molecule, and we suggest that it has been formed by cycloaddition of a second molecule of $Ru(C \equiv CC \equiv CH)(dppe)Cp^*$ to 8 followed by ring-opening. Indeed, reaction of pure 8 with $Ru(C \equiv CC \equiv CH)(dppe)Cp^*$ gives 9 in high yield. Formally, this reaction corresponds to insertion of the C \equiv CH triple bond into the =C-H bond present in 8. Double addition of TCNE has been observed previously for $\{Ru(PPh_3)_2Cp\}_2(\mu-C_8)$ to give $\{Cp(Ph_3P)_2Ru\}_2$ $C \equiv C \{C [= C(CN)_2]\}_4 C \equiv C \{Ru(PPh_3)_2 Cp\}^{37}$ but this is the first occasion on which addition of two metal fragments to a single cyanocarbon molecule has been demonstrated. In principle, this mode of action should be available to other tetracyanobutadiene complexes. As mentioned above, various octacyano[4]dendralenes were formed by double addition of TCNE to anilino-capped buta-1,3-diynes,²² and cascade additions of TCNE and tetrathiafulvene to $4-Me_2NC_6H_4(C \equiv$ C), Ph have been described.²³ Reactions of Ph-diynyl- or Phtriynyl-ruthenium complexes with TCNQ afford products 10-**Ru** and **11**, in which the cvanocarbon has added to the $C \equiv C$ triple bond one removed from the metal center; the iron analogue 10-Fe has been obtained from a similar reaction with 6-Fe.

The molecular structures of the new complexes described above have been confirmed by single-crystal X-ray diffraction studies. Of note is the twisting of the butadiene moiety, with dihedrals between the two C=C double bonds ranging between 12.6(4)° (for 9) and 73.6(2)° (for 10-Ru). In analogous tricyanovinyl organics this feature has been related to a preference for π conjugation with other substituents rather than with the second C=C double bond in the usual diene structure.^{5c} In the present cases (and those found with TCNE earlier),^{15a} this may be related to charge transfer from the electron-rich metal center to give a stable zwitterionic vinylidene mesomer of the complex, the formation of which would be encouraged by delocalization of electron density onto the C(CN)₂ groups.

There is an interesting contrast between the reactions of TCNQ with similar iron complexes, which afford the oxidized (1-e) compounds, and a richer chemistry found with the ruthenium systems. These results further highlight the

differences in electronic structures of the two series of complexes. DFT calculations have shown that the Fe complexes have a high tendency for electron density in the HOMOs to be centered on the metal atom. In the Ru analogues, higher coefficients are found on the carbon atoms of the chain.³⁸ Evidently, for the phenylethynyl complex, loss of an electron from the iron center to generate the related 17-e cation is preferred over extended conjugation with the unsaturated chain, which leads to formation of more electron-rich centers that can attack the cyanocarbon at the $=C(CN)_2$ groups. On the other hand, lengthening of the C(sp) chain allows the iron and ruthenium systems to display similar chemistry, as found here for $M(C \equiv CC \equiv CPh)(dppe)Cp^*$ (M = Fe, Ru).²⁵

In conclusion, the first step in all of these reactions appears to be electron transfer from the metal to the cyanocarbon, generating structure **G** (Scheme 2). If the steric protection within the radical is large enough, the cationic complex is stable enough to isolate. This is particularly the case when there is a single $C \equiv C$ bond. With poly-ynyl derivatives, delocalization of the spin density on the poly-ynyl ligand is larger and C-C bond formation can ensue. When this occurs, formation of cyclobutenyl and butadienyl derivatives is found.

Detailed examination of the structural parameters of complexes described above and related systems reported elsewhere points to significant contributions from zwitterionic forms of the molecules. Of interest in this discussion are (a) the lengths of the M–P, M–C(1), and C(1)–C(2) bonds and (b) the degree of quinoid character possessed by the $=C_6H_4=$ $C(CN)_2$ fragment. Characteristic lengths for Ru–C(sp) bonds in alkynyl complexes are ca. 2.000 Å [cf. 2.015(2) Å in Ru(C≡ CH)(dppe)Cp*²⁸], while for Ru=C(sp) bonds in vinylidenes, distances of ca. 1.85 Å [cf. 1.85(1) Å in $[Ru(=C=C_2)(dppe)Cp^*]^{+38b}$] are found. In the molecules derived from TCNQ whose structures are reported here and elsewhere,²¹ the Ru-C distances range between 1.855(6) Å in 12 (Chart 1) and 1.943(4) Å in 9 and 10-Ru. All are considerably shorter than the Ru-C(sp) single bond, but approach the value expected for a Ru=C(sp) double bond in vinylidenes. The Ru-P distances fall within the range 2.26 Å (found for neutral Ru-alkynyl complexes)²⁸ to 2.36 Å (found in cationic Ruvinylidene complexes).^{38b} These data suggest that there is a considerable contribution from the mesomeric zwitterionic structure, with charge separation between the positively charged metal center and the anion stabilized by the distant cyanocarbon group (Scheme 5). This will have a further effect upon the geometry of the $=C_6H_4=C(CN)_2$ group, which will tend toward the fully aromatic structure. Further, in the case of 10-Fe, Fe-P bond distances also support a zwitterionic structure, while Mössbauer spectroscopy clearly confirms that this structure is strongly dominant.

Comparison of the structural parameters of TCNQ itself³⁹ with those of the various fragments found in these complexes is instructive. In TCNQ, the two exocyclic C=C(CN)₂ groups have C=C, C-CN, and C=N bond lengths of 1.374(3), 1.440(3), and 1.141(3) Å, respectively.⁴² Within the C₆ ring, the C=C and C-C bonds are 1.346(3) and 1.450(3) Å. As charge accumulates on the C₆H₄=C(CN)₂ group, transformation of the C₆H₄ moiety toward a fully aromatic structure occurs. The quinoid character of C₆ rings, δr , can be expressed by



For benzene δr is 0 Å, but increases to ca. 0.08–0.10 Å for quinoid rings; for TCNQ itself, δr is 0.102 Å.^{38a} The detailed results are given in Table S1 (Supporting Information), which includes values for δr . Only in 13 (Chart 1) does this value (0.093 Å) approach that of TCNQ itself, while in 12, in which the C₆ ring originating in TCNQ has become fully aromatic, δr is 0.012 Å. In the other complexes listed in Table S1 (1, 8, 9, 10-Fe, 10-Ru, and 11), the values range between 0.031 and 0.066 Å. For 8, the low value of 0.031 Å relates to short C-Cbond average (c + c')/2 of 1.398(0) Å, the value for (a + a')being 1.444(0) Å. The decrease in δr is the result of replacing the strong acceptor $C = C(CN)_2$ group by the electron-rich group 8 metal center, which acts as a strong donor. Values of δr can in turn be related to the Ru–P and Ru=C bond lengths, thus giving a second estimate of the contribution of the quinoid character to the structure. Further, in CT salts, the apparent charge per TCNQ anion can be determined from the exocyclic double-bond lengths.^{40,41} As summarized in Table S1, the single exocyclic C=C lengths range from 1.39(2) Å (for 8) to 1.454(15) Å (for 1).

CONCLUSIONS

In this paper we have extended our earlier study of the reactions of TCNQ with alkynyl-iron and -ruthenium complexes²¹ to those of analogous diynyl and triynyl systems. In the case of $Ru(C \equiv CC \equiv CH)(dppe)Cp^*$, the product $Ru{C \equiv CC[=C_6H_4=C(CN)_2]CH=C(CN)_2}(dppe)Cp^*$ (8) is formed by ring-opening of the initial [2 + 2]-adduct of TCNQ to the outer $C \equiv C$ triple bond. A second equivalent of the diynyl-Ru complex adds to a C=C double bond of 8 (possibly via initial formation of charge-transfer and zwitterionic intermediates) to give binuclear $\{Ru(dppe)Cp^*\}$ $CC[=C_6H_4=C(CN)_2]CH=CHC[=C(CN)_2]C\equiv C$ {Ru-(dppe)Cp*} (9). The latter reaction is unprecedented in the otherwise similar chemistry of TCNE. Iron and ruthenium complexes M(C=CC=CPh)(dppe)Cp* react to give analogous η^1 -(butadienyl)ethynyls {C = CC[=C_6H_4=C(CN)_2]- $CPh=C(CN)_2$ (dppe) Cp^* (10-M); a similar reaction with the analogous triynyl-Ru precursor affords Ru{C=CC[= $C_{6}H_{4} = C(CN)_{2}C(C = CPh) = C(CN)_{2}(PPh_{3})_{2}Cp$ (11). The molecular structures of the new complexes have been determined by single-crystal X-ray diffraction studies. The structural parameters give information about the degree of charge transfer from the electron-rich M(PP)Cp' group to the TCNQ-derived ligands. In this process, the alkynylmetal moiety takes on some vinylidene character (shorter M-C, longer M-P, and C \equiv C bonds), while the quinodimethane portion, of which the $=C(CN)_2$ group can accept charge, becomes more aromatic, as measured by the endocyclic C=C distances. The chromophores in all complexes described show interesting CT behavior, the complexes themselves being further examples of interesting donor-acceptor molecular arrays.

EXPERIMENTAL SECTION

General Procedures. All reactions were carried out under dry nitrogen, although normally no special precautions to exclude air were taken during subsequent workup. Common solvents were dried, distilled under nitrogen, and degassed before use. Separations were carried out by preparative thin-layer chromatography on glass plates $(20 \times 20 \text{ cm}^2)$ coated with silica gel (Merck, 0.5 mm thick).

Instruments. IR spectra were obtained on a Bruker IFS28 FT-IR spectrometer. Spectra in CH₂Cl₂ were obtained using a 0.5 mm pathlength solution cell with NaCl windows. NMR spectra were recorded on a Varian Gemini 2000 instrument (¹H at 300.145 MHz, ¹³C at 75.479 MHz, ³¹P at 121.501 MHz). Unless otherwise stated, samples were dissolved in CDCl₃ contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane for ¹H and ¹³C NMR spectra and external H₃PO₄ for ³¹P NMR spectra. UV-vis spectra were recorded on a Varian Cary 5 UV-vis/NIR spectrometer. Electrospray mass spectra (ES-MS) were obtained from samples dissolved in MeOH unless otherwise indicated. Solutions were injected into a Varian Platform II spectrometer via a 10 mL injection loop. Nitrogen was used as the drying and nebulizing gas. Chemical aids to ionization were used as required.⁴³ The ⁵⁷Fe Mössbauer spectra were recorded with a 2.5×10^{-2} C (9.25 × 108 Bq) ⁵⁷Co source using a symmetric triangular sweep mode. Computer fitting of the Mössbauer data to Lorentzian line shapes was carried out with a previously reported computer program.³¹ The isomer shift values are reported relative to iron foil at 298 K. Elemental analyses were by Campbell Microanalytical Laboratory, University of Otago, Dunedin, New Zealand.

Reagents. $Ru(C \equiv CC \equiv CH)(dppe)Cp^{*,44}$ $M(C \equiv CC \equiv CPh)(dppe)Cp^{*}$ (M = Fe, Ru),³⁶ and $Ru(C \equiv CC \equiv CC \equiv CPh)(PPh_{3})_{2}Cp^{36}$ were made by the literature methods. TCNQ was a commercial sample (Aldrich).

Reactions of TCNQ. *i. With* $Ru(C \equiv CC \equiv CH)(dppe)Cp^*$. *a. In* THF. THF (8 mL) was added to a Schlenk flask containing $Ru(C \equiv$ CC≡CH)(dppe)Cp* (5) (50 mg, 0.073 mmol) and TCNQ (18 mg, 0.088 mmol) to give a dark green solution. After 2 h at room temperature, solvent was removed and the residue was purified by preparative TLC (acetone/hexane, 3/7). The green band ($R_f = 0.41$) was collected to afford $Ru\{C \equiv CC = C_6H_4 = C(CN)_2\}$ CH=C- $(CN)_2]\}(dppe)Cp^{\ast}\ (8)\ (6$ mg, 9%) as a dark green solid. X-ray quality crystals were obtained from benzene/hexane. Anal. Calcd (C₅₂H₄₄N₄P₂Ru): C, 70.34; H, 4.99; N, 6.31; M, 888. Found: C, 70.74; H, 5.16; N, 6.50. IR (CH₂Cl₂, cm⁻¹): ν (C \equiv N) 2193w, ν (C \equiv C) 1940s, ν (C=C) 1586 m. ¹H NMR (C₆D₆): δ 1.38 (s, 15H, Cp*), 1.94, 2.57 (2m, 4H, CH2), 6.72 [s, 1H, CH=C(CN)2], 7.01-7.42 (m, 24H, Ph). ¹³C NMR (C_6D_6): δ 9.79 (s, C_5Me_5), 29.42–30.30 (m, dppe), 86.13 (s), 96.61 (s, C₅Me₅), 111.73, 113.89, 117.53, 120.89 (4s, CN), 124.75-138.22 (m, Ph), 145.01 (s), 152.70 (s), 155.26 (s), 218.70 [t, ${}^{2}J_{CP}$ = 23 Hz, Ru-C \equiv]. ${}^{31}P$ NMR (C₆D₆): δ 80.4 (s). ES-MS (MeOH/NaOMe, *m*/*z*): found 888.2128, M⁺ (calcd 888.2085).

b. In C_6H_6 . To a solution of Ru(C=CC=CH)(dppe)Cp* (5) (50 mg, 0.073 mmol) in benzene was added TCNQ (15 mg, 0.073 mmol); the solution turned slowly from yellow to dark green. After 2 h at room temperature, solvent was removed and the residue was purified by preparative TLC (acetone/hexane, 3/7). The brown band (R_f = 0.38) was collected to afford {Ru(dppe)Cp*}{C = C_6H_4 = C_6H_4 $C(CN)_2$ CH=CHC[= $C(CN)_2$]C=C}{Ru(dppe)Cp*} (9) (6 mg, 10%) as a dark brown solid. X-ray quality crystals were obtained from benzene/diethyl ether. Anal. Calcd (C92H84N4P4Ru2): C, 70.30; H, 5.39; N, 3.56; M, 1572. Found: C, 70.01; H, 5.59; N, 3.52. IR $(CH_2Cl_2, cm^{-1}): \nu(C \equiv N)$ 2186w, $\nu(C \equiv C)$ 1983s, 1947s, $\nu(C = C)$ 1579 m. ¹H NMR (C₆D₆): δ 1.51 (s, 15H, Cp*), 1.53 (s, 15H, Cp*), 1.99-2.12 (m, 4H, 2 × CH₂), 2.68, 2.82 (2 m, 4H, 2 × CH₂), 6.88-7.63 (m, 46H, Ph and HC=CH). ¹³C NMR (C_6D_6): δ 10.28 (s, C₅Me₅), 10.41 (s, C₅Me₅), 29.31-30.91 (m, dppe), 77.10 (s), 95.56 (s, C₅Me₅), 96.62 (s, C₅Me₅), 114.43, 117.49, 118.05, 118.95 (4s, CN), 121.17 (s), 127.52–153.58 (m, Ph), 191.89, 210.57 [2 × t(br), Ru- $C \equiv$]. ³¹P NMR (C₆D₆): δ 80.7 (s), 81.8 (s). ES-MS (MeOH/ NaOMe, m/z): found 1573.3752, $[M + H]^+$ (calcd 1573.3812).

c. Independent Synthesis of **9**. When THF was added to a Schlenk flask containing $\operatorname{Ru}(C \equiv CC \equiv CH)(\operatorname{dppe})Cp^*$ (**5**) (5 mg, 0.007 mmol) and $\operatorname{Ru}\{C \equiv CC [= C_6H_4 = C(CN)_2]CH = C(CN)_2\}(\operatorname{dppe})-Cp^*$ (**8**) (6 mg, 0.007 mmol), a dark brown solution was formed immediately. After 1 h at room temperature, solvent was removed and the residue was purified by preparative TLC (acetone/hexane, 3/7). The brown band ($R_f = 0.38$) contained {Ru(dppe)Cp^*}{C \equiv CC[= C_6H_4 = C(CN)_2]CH = CHC[= C(CN)_2]C \equiv C}{Ru(dppe)Cp^*} (**9**) (6 mg, 56%).

ii. With $Fe(C \equiv CC \equiv CPh)(dppe)Cp^*$. THF (15 mL) was added to a Schlenk flask containing Fe(C=CC=CPh)(dppe)Cp* (6-Fe) (200 mg, 0.280 mmol) and TCNQ (57 mg, 0.280 mmol) at -78 °C to give a dark purple solution. After 1 h at -78 °C, the solution was allowed to warm to room temperature over 4 h. Pentane (50 mL) was then added to the solution, and the purple precipitate was filtered off and washed with pentane $(3 \times 10 \text{ mL})$ to afford Fe{C=C-C[=C_6H_4= $C(CN)_2$ CPh= $C(CN)_2$ (dppe) Cp* (10-Fe) (184 mg, 71%) as a dark purple solid. X-ray quality crystals were obtained from $CH_2Cl_2/$ pentane. Anal. Calcd (C₅₈H₄₈N₄P₂Fe·0.33CH₂Cl₂): C, 73.97; H, 5.18; N, 5.92; M, 918. Found: C, 74.28; H, 5.18; N, 5.83. IR (KBr): *ν*(C≡ N) 2223w, 2183w, $\nu(C \equiv C)$ 1914s, $\nu(C = C)$ 1579 m cm⁻¹. ¹H NMR: δ 1.21 (s, 15H, Cp*), 1.76-2.42 (m, 4H, PCH₂), 6.85-7.60 (m, 29H, Ph). ¹³C NMR: δ 9.52 (s, C₅Me₅), 30.87 [t, ¹J_{PC} = 22 Hz, dppe], 82.39 (s), 96.54 (s, C₅Me₅), 112.85, 113.01, 120.30, 121.14 (4s, CN), 127.86-136.97 (m, Ph), 150.95 (s), 170.97 (s), 178.01 (s), 244.90 [t, ${}^{2}J_{PC}$ = 35 Hz, Ru-C=]. ³¹P NMR: δ 94.3 (s). ES-MS (m/z): found 919.2786, [M + H]⁺ (calcd 919.2782).

iii. With Ru(C=CC=CPh)(dppe)Cp*. When THF (8 mL) was added to a Schlenk flask containing Ru(C=CC=CPh)(dppe)Cp* (6-Ru) (53 mg, 0.070 mmol) and TCNQ (16 mg, 0.077 mmol), the solution became dark blue instantaneously. After 1 h at rt, solvent was removed and the residue was taken up in a small amount of CH₂Cl₂ and purified by chromatography (acetone/hexane, 3/7, silica gel) to afford $Ru{C \equiv CC[=C_6H_4 = C(CN)_2]CPh = C(CN)_2}(dppe)Cp^*$ (10-Ru) (49 mg, 73%) as a dark blue solid ($R_f = 0.11$). X-ray quality crystals were obtained from CH2Cl2/C6H6. Anal. Calcd $(C_{58}H_{48}N_4P_2Ru)$: C, 72.26; H, 5.02; N, 5.81; M, 964. Found: C, 71.74; H, 5.11; N, 5.63. IR (CH_2Cl_2/cm^{-1}) : $\nu(C\equiv N)$ 2194w, $\nu(C\equiv N)$ C) 1946s, ν (C=C) 1585 m. ¹H NMR: δ 1.53 (s, 15H, Cp*); 2.22 (m, 4H, CH₂); 6.96–7.50 (m, 29H, Ph). ¹³C NMR: δ 10.24 (s, C₅Me₅), 30.01–30.62 (m, dppe), 58.28 (s), 83.18 (s), 98.17 (s, C₅Me₅), 113.03, 113.50, 121.33, 123.20 (4s, CN), 128.38-137.47 (m, Ph), 150.24 (s), 153.81 (s), 171.56 (s), 217.10 (br, Ru- $C\equiv$). ³¹P NMR: δ 80.5 [br d, $J_{\rm PP} = 113.5 \text{ Hz}$]. ES-MS (MeOH/NaOMe, m/z): 965, $[M + H]^+$; 987, $[M + Na]^+$.

iv. With Ru(C=CC=CC=CPh)(PPh_3)_2Cp. TCNQ (41 mg, 0.2 mmol) was added to a solution of $Ru(C \equiv CC \equiv CC \equiv CPh)$ -(PPh₃)₂Cp (7) (168 mg, 0.2 mmol) in CH₂Cl₂ (20 mL), resulting in an instantaneous darkening of the solution. After 1 h solvent was reduced to approximately 1 mL and hexane (50 mL) was added to give a dark blue precipitate. The precipitate was collected and then washed with diethyl ether (10 mL) to afford $Ru\{C \equiv CC[=C_6H_4=$ $C(CN)_2$ C(C=CPh)=C(CN)_2 (PPh_3)_2 Cp (11) (183 mg, 88%) as a dark blue solid. X-ray quality crystals were grown from dichloromethane/MeCN. Anal. Calcd (C₆₅H₄₄N₄P₂Ru): C, 74.77; H, 4.25; N, 5.37; *M*, 1044. Found: C, 74.18; H, 4.86; N, 5.19. IR (CH₂Cl₂, cm⁻¹): $\nu(\text{C}{\equiv}\text{N})$ 2198w, $\nu(\text{C}{\equiv}\text{C})$ 1956s, $\nu(\text{C}{=}\text{C})$ 1590 m. ¹H NMR: δ 4.64 (s, 5H, Cp); 7.01–7.52 (m, 39H, Ph). ¹³C NMR: δ 61.77 (s), 86.75 (s), 88.86 (s, Cp), 90.32 (s), 111.86 (s), 112.90, 113.46 (2s, CN), 117.69 (s), 119.91 (s), 121.49, 123.55 (2s, CN), 127.98-136.80 (m, Ph), 146.99 (s), 153.86 (s), 154.05 (s), 217.99 [t, ${}^{2}J_{CP} = 23$ Hz, Ru-C=]. ³¹P NMR: δ 48.0 (s). ES-MS (MeOH/NaOMe, m/z): found 1045.2221, [M + H]⁺ (calcd 1045.2163).

Structure Determinations. Diffraction data were measured using Oxford Diffraction Xcalibur CCD diffractometers (Oxford Diffraction Gemini for 8, Bruker-AXS APEXII for **10-Fe**) at 100 K with Mo K α radiation, $\lambda = 0.71073$ Å (Cu K α , $\lambda = 1.54184$ Å for 8). Following multiscan absorption corrections and solution by direct methods, the structures were refined using full-matrix least-squares refinements on F^2 using the SHELXL-97 program.^{45–47} Except where stated below,

Table 4. Crystal Data and Refinement Details

	8	9	10-Fe	10-Ru	11
CCDC #	835455	835456	892450	835457	835458
formula	$C_{52}H_{44}N_4P_2\;Ru{\cdot}0.25C_6H_6$	$\substack{C_{92}H_{84}N_4P_4\\Ru_2\cdot C_4H_{10}O\cdot C_6H_6}$	$C_{58}H_{48}N_4P_2 \ Fe{\cdot}CH_2Cl_2$	$C_{58}H_{48}N_4P_2 Ru \cdot 3C_6H_6$	$C_{65}H_{44}N_4P_2\ Ru{\cdot}1.5CH_2Cl_2$
MW	907.45	1723.88	1003.72	1198.34	1171.44
cryst syst	triclinic	triclinic	triclinic	monoclinic	triclinic
space group	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$	P2 ₁	$P\overline{1}$
a/Å	12.5353(6)	10.9127(5)	13.0027(6)	14.0764(10)	14.1999(3)
b/Å	25.7160(10)	16.6873(6)	13.5494(6)	12.1829(8)	14.9393(3)
c/Å	29.3469(15)	24.4436(11)	15.2633(8)	18.9165(14)	15.1754(3)
α/deg	76.344(4)	94.234(3)	69.676(2)		65.886(2)
β /deg	81.617(4)	94.875(4)	84.497(2)	100.112(7)	80.367(2)
γ/deg	80.015(4)	105.793(3)	88.105(2)		69.633(2)
$V/Å^3$	8999.0(7)	4245.9(3)	2510.0(2)	3193.6(4)	2753.4(1)
$ ho_{\rm c}/{\rm g~cm^{-3}}$	1.34	1.348	1.328	1.246	1.413
Z (f.u.)	8	2	2	2	2
$2\theta_{\rm max}/{ m deg}$	134	56	55	50	78
μ (Mo K $lpha$)/mm ⁻¹	3.80 (Cu Kα)	0.48	0.51	0.34	0.54
transmn (min./max.)	0.29/0.71	0.96/0.99	0.83/0.97	0.78/0.95	0.85/0.87
cryst dimens/mm ³	$0.27\times0.04\times0.03$	$0.15 \times 0.06 \times 0.05$	$0.20\times0.18\times0.07$	$0.49 \times 0.33 \times 0.14$	$0.32\times0.31\times0.27$
reflns measd	67 492	34 953	34 753	21 911	76 060
unique reflns (R_{int})	28728 (0.233)	20508 (0.050)	11445 (0.064)	10555 (0.036)	31399 (0.033)
reflns $(I > 2\sigma(I)]$	12 545	15 480	8652	9667	23 425
$R_1 \left[I > 2\sigma(I) \right]$	0.165	0.072	0.059	0.067	0.043
wR_2 (all data)	0.426	0.136	0.121	0.149	0.115

anisotropic displacement parameter forms were refined for the nonhydrogen atoms; hydrogen atoms were treated with a riding model. Pertinent results are given in Figures 1-4 (which show non-hydrogen atoms with 50% probability amplitude displacement ellipsoids, with hydrogen atoms removed for clarity) and in Tables 1 and 4.

8: Crystals of 8 were thin needles that diffracted very poorly. Even though the data were collected over several days using the intense Enhance Ultra Copper tube of the Oxford Diffraction diffractometer, the resultant data set was weak and of limited resolution. This resulted in a low fraction of "observed" reflections (12 545 out of 28 728 with $I > 2\sigma(I)$) and a high R(int). Only the Ru and P atoms were refined with anisotropic displacement parameters. The crystal structure nevertheless does identify the molecule unambiguously, albeit with high uncertainties in the geometries.

9: One Ph ring and its associated CH_2 atoms of one dppe ligand were modeled as being disordered over two sets of sites with occupancies constrained to 0.5 after trial refinement.

ASSOCIATED CONTENT

Supporting Information

Tables S1 (bond lengths and angles for TCNQ derivatives: δr calculations). Crystallographic data in CIF format for the compounds studied by X-ray diffraction. This material is available free of charge via the Internet at http://pubs.acs.org. Full details of the structure determinations (except structure factors) have also been deposited with the Cambridge Crystallographic Data Centre as CCDC 835455–835458, 892450. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: + 44 1223 336 033; e-mail: deposit@ccdc. cam.ac.uk; or www: http://www.ccdc.cam.ac.uk).

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge financial support of this work by the ARC (Australia) and the CNRS (France). A.B. gratefully acknowledges le Ministère de l'Enseignement Supérieur et de la Recherche (France) for a Ph.D. grant. M.I.B. thanks Johnson Matthey plc for a generous loan of RuCl₃·nH₂O. L'Université Européenne de Bretagne is acknowledged for a travel grant to A.B.

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