# **ORGANOMETALLICS**

# Substitution of Tetracyanoethene by Ethynyl–Metal Complexes Gives Tricyanovinylethynyl (Tricyanobutenynyl) Derivatives: Syntheses, Protonation, and Addition of Metal–Ligand Fragments

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#### **S** Supporting Information

**ABSTRACT:** A series of complexes containing the new tricyanovinylethynyl (3,4,4-tricyanobut-3-en-1-ynyl) ligand have been obtained by substitution of a CN group in tetracyanoethene upon reaction with the ethynyl complexes  $M(C \equiv CH)(PP)Cp'$  (M = Ru, Os, (PP)Cp' =  $(PPh_3)_2Cp$ ; M = Ru, PP = dppe, Cp' = Cp, Cp\*). The reactions proceed in higher yield as the metal environment becomes more sterically hindered, the normal [2 + 2]-cycloaddition/ring-opened product  $M\{C[=C(CN)_2]CH=C(CN)_2\}(PP)Cp'$  also being formed in some cases. The diynyl complex Ru(C $\equiv$ CC $\equiv$ CH)(dppe)Cp\* reacts with tcne to give only the ring-opened adduct Ru{C $\equiv$ CC[=C-(CN)\_2]CH=C(CN)\_2}(dppe)Cp\*. Protonation (HBF<sub>4</sub> or HPF<sub>6</sub>) of Ru{C $\equiv$ CC(CN)=C(CN)\_2}(dppe)Cp\* afforded the vinylidene cation [Ru{=C=CHC(CN)=C(CN)\_2}(dppe)Cp\*]<sup>+</sup>. A second transitionmetal fragment ML<sub>n</sub> (ML<sub>n</sub> = Ru(PPh\_3)\_2Cp, M'(dppe)Cp\* (M' = Ru,



Os), RuCl(dppe)<sub>2</sub>) can be added to the CN group trans to the metal center; electrochemical, spectroscopic, and computational studies indicate that there is little ground-state delocalization between the metal centers. In the case of the tricyanovinylethynyl derivatives, an intense MLCT (or ML—LCT) transition can be identified in the visible region, which is responsible for the intense blue to purple color of these species; the analogous transition in the vinylidene-based complexes is significantly blue-shifted. The X-ray crystallographically determined structures of several of these complexes are reported. The cations  $[{Cp*(dppe)Ru}{\mu-(C/N)\equiv CC(CN)=C(CN)(\equiv C/N)}{M(dppe)Cp*}]^+ (M = Ru, Os)$  show some  $C\equiv C/C\equiv N$  disorder (and associated Ru/Os disorder in the case of the heterometallic example) in the crystals.

## INTRODUCTION

Since its discovery,<sup>1</sup> the chemistry of tetracyanoethene (tcne),  $(NC)_2C=C(CN)_2$ , has provided numerous examples of novel addition and substitution reactions.<sup>2</sup> For example, tcne readily undergoes Diels–Alder reactions with dienes, while one or two CN groups may be substituted by alcohols, thiols, or aromatic amines, to give 2,2-dicyanoketene acetals and thioacetals and tricyanovinylanilines, respectively. The formation of  $\pi$  complexes between tcne and a variety of unsaturated (usually aromatic) hydrocarbons affords materials with intense charge-transfer absorptions in their visible–UV spectra. Several extensive reviews of the chemistry of this remarkable olefin are available.<sup>3,4</sup>

The transition-metal chemistry of tcne is also rich and has afforded several surprises. With two potential donor sites (CN

and C=C), metal complexes were readily obtained, coordination of CN groups to metal centers being the more commonly observed bonding mode. Recent examples include Ru( $\eta^1$ tcne){NBu<sup>t</sup>=C(mes)NBu<sup>t</sup>}Cp<sup>\*</sup>,<sup>5</sup> trans-[{Ru(PPh\_3)\_2Cp}\_2( $\mu$ tcne)]<sup>2+,6</sup> and [{Fe(CO)\_2Cp}\_4( $\mu_4$ -tcne)]<sup>n+</sup> (n = 3, 4).<sup>7</sup> Metal  $\pi$  complexes were first reported by Baddley, who prepared Pt{ $\eta^2$ -C<sub>2</sub>(CN)<sub>4</sub>}(PPh\_3)\_2 and showed conversion of this complex to trans-Pt(CN){C(CN)=C(CN)\_2}(PPh\_3)\_2.<sup>8,9</sup> Many related compounds have since been prepared, especially for the later transition metals, such as M(CO)<sub>5</sub>( $\eta^2$ -tcne)

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Received: August 11, 2011 Published: November 1, 2011 (M = Cr, W),<sup>10</sup> Ru( $\eta^2$ -tcne)(NR=CR'NR)Cp\*,<sup>5</sup> and M( $\eta^2$ -tcne)(L)<sub>2</sub> (M = Ni, Pd, Pt, L = CNAr),<sup>11</sup> and aspects of the coordination chemistry of tcne and physical properties of the resulting complexes have also been reviewed.<sup>12-14</sup>

[2 + 2]-Cycloaddition of tcne to electron-deficient alkenes to give cyclobutenes was first described by Hopf and co-workers,<sup>15</sup> and more recently, the elegant studies of Diederich and his group have given a series of compounds with interesting push–pull electronic properties.<sup>16</sup> Similar tetracyanocyclobutenyls were obtained earlier from reactions of transition-metal alkynyls and were observed to undergo more or less ready ring-opening reactions to form tetracyanobutadienyl complexes (Scheme 1),<sup>17,18</sup>

Scheme 1. [2 + 2]-Cycloaddition of  $C_2(CN)_4$  to Alkynyl– Transition Metal Complexes and Subsequent Retro-Cyclization and Ligand Displacement Reactions<sup>18a</sup>



which are sensitive to a range of further reactions.<sup>19</sup> In studies aimed at extending the [2 + 2]-cycloaddition reaction to the parent ethynyl complexes, such as Ru(C=CH)(PPh<sub>3</sub>)<sub>2</sub>Cp, we have now found that a competing reaction is the replacement of one of the CN groups by the alkynyl group, with elimination of HCN, to give unprecedented tricyanovinylethynyl (1,1,2tricyanobut-1-en-3-yn-4-yl) complexes, such as Ru{C=CC-(CN)=C(CN)<sub>2</sub>}(PPh<sub>3</sub>)<sub>2</sub>Cp.<sup>20</sup> Previous accounts of tricyanovinyl complexes are sparse, with MCl{C(CN)=C(CN)<sub>2</sub>}(PP)<sub>2</sub> (M = Fe, Ru, Os; PP = dmpe, dppe),<sup>21</sup> Fe{C(CN)=C(CN)<sub>2</sub>}-(CO)<sub>2</sub>Cp,<sup>22</sup> PdCl{C(CN)=C(CN)<sub>2</sub>}(bpy),<sup>23</sup> and PtH{C-(CN)=C(CN)<sub>2</sub>}(PCy<sub>3</sub>)<sub>2</sub><sup>24</sup> having been described. However, to our knowledge, no examples of tricyanovinylethynyl ligands exist. The CN groups in these complexes are reactive, showing ability to act as coordinating sites toward other metal–ligand fragments, and have a propensity for substitution by other nucleophiles. Some of these results have been described in a preliminary account.<sup>20</sup>

#### RESULTS

Reactions of tcne with Ethynyl–Ruthenium and –Osmium Complexes. In seeking to prepare the parent tetracyanobutadienyl complex  $Ru{C[=C(CN)_2]CH=C(CN)_2}(PPh_3)_{2}Cp$ 

(1-Ru), the reaction between  $Ru(C \equiv CH)(PPh_3)_2Cp$  and tone was carried out in tetrahydrofuran at room temperature for 2 h. Conventional workup of the burgundy reaction mixture afforded red 1-Ru in 64% yield, accompanied by a purple product, identified as the tricyanovinylethynyl complex  $Ru{C \equiv CC(CN) = C(CN)_2}(PPh_3)_2Cp$  (2-Ru), which was isolated in 10% yield. 1-Ru is unstable in solution toward loss of PPh<sub>3</sub>: it is likely that the corresponding  $\eta^3$ -butadienyl complex is produced, although we did not isolate this compound. The facile conversion of  $\eta^{1}$ - to  $\eta^{3}$ -butadienyls with concomitant loss of one PPh<sub>3</sub> ligand is a common reaction of compounds containing the Ru(PPh<sub>3</sub>)<sub>2</sub>Cp fragment.<sup>18c,19,25</sup> The analogous osmium complexes 1-Os (which is more stable than the ruthenium analogue) and **2-Os** were obtained similarly from tcne and  $Os(C \equiv CH)(PPh_3)_2Cp$  in 30 and 22% yields, respectively. Replacement of the PPh<sub>3</sub> ligands in the ethynylruthenium precursor by dppe resulted only in formation of the corresponding tetracyanobutadienyl complex, Ru{C[=C- $(CN)_2$ ]CH=C(CN)\_2 (dppe)Cp (3). Of note in the <sup>31</sup>P NMR spectrum of 3 is the appearance of two broad signals at  $\delta_{\rm p}$  72.6 and 82.3, which are resolved into two doublets at  $\delta_{\rm p}$ 68.9 and 80.8 (I(PP) = 23 Hz) upon cooling to -57 °C. The smaller steric bulk of the dppe ligand allows restricted rotation of the cyanocarbon ligand about the Ru-C bond, this process being precluded for the analogous PPh<sub>3</sub> complex 1.

Deprotonation of the vinylidenes  $[Ru(=C=CH_2)(PP)Cp]$ - $PF_6$  (PP = (PPh<sub>3</sub>)<sub>2</sub>, dppe) with 2 equiv of an alkyllithium base (both LiMe or LiBu being effective) to give the putative acetylide salts  $Li[Ru(C \equiv C)(PP)Cp]$ ,<sup>26</sup> followed by addition of tcne, gave  $Ru\{C \equiv CC(CN) = C(CN)_2\}(PP)Cp(PP = (PPh_3)_2)$ 2-Ru (37%), dppe 4 (69%)). Given the facile substitution of CN<sup>-</sup> by strongly nucleophilic reagents,<sup>3,4</sup> such reactions are perhaps to be expected. In contrast, the complex Ru{C=  $CC(CN) = C(CN)_2 (dppe) Cp^*$  (5) was the only product from the reactions between tcne and Ru(C≡CH)(dppe)Cp\* (93%). The greater electron-donating properties of the Ru(dppe)Cp\* moiety, and hence greater nucleophilicity of the  $C_{\beta}$  carbon, together with the increased steric congestion of the alkynyl moiety which limits formation of the intermediate [2 + 2]-cycloadduct en route to the  $\eta^1$ -butadienyl isomer, are likely to be responsible for this shift in reactivity profile. Similar results were also obtained from the reaction of [Ru(=C= $CH_2$  (dppe)  $Cp^*$  PF<sub>6</sub>/2LiMe with tcne, 5 being formed in similar yield (95%). The conventional tetracyanobutadienylethynyl complex  $Ru{C \equiv CC[=C(CN)_2]CH = C(CN)_2}$ - $(dppe)Cp^*$  (6) was obtained from the reaction between tone and  $Ru(C \equiv CC \equiv CH)(dppe)Cp^*$ , being formed by addition of the cyanoalkene to the outer  $C \equiv C$  triple bond, followed by ring opening. This chemistry is summarized in Scheme 2.

Most of the new complexes have been characterized by single-crystal X-ray diffraction structure determinations, as described earlier for 1 and 2-Os<sup>20</sup> and herein for 2-Ru and 3– 5. Plots of single molecules of 2-Ru, 4, and 5 are shown in Figures 1–3, while selected structural data are collected in Table 1. The usual pseudo-octahedral M(PP)Cp fragments (Ru-C(cp) = 2.217(5)-2.292(5) Å (average 2.231(10)–2.271(16) Å), Ru-P = 2.260(1)-2.3211(3) Å) are attached to the tricyanovinylethynyl ligand by C(1) (Ru-C(1) = 1.920(1)-1.930(3) Å), although there are considerable differences contingent upon the change from mono- to bidentate phosphine(s). The C-C separations along the C<sub>4</sub> chain (C(1)-C(2) = 1.224(5)-1.243(7) Å, C(2)-C(3) = 1.378(2)-1.388(8) Å, C(3)-C(4) = 1.368(8)-1.391(5) Å) Scheme 2. Addition of  $C_2(CN)_4$  to Ethynyl- and Butadiynyl-Metal Complexes



are consistent with C=C triple,  $C(sp)-C(sp^2)$  single, and  $C(sp^2)=C(sp^2)$  double bonds, respectively, with angles at C(n) being 169.82(8)-179.5(3)° (n = 1), 172.3(1)-173.5(4)° (n = 2) and 124.3(1)-126.3(6)° (n = 3). Of interest are the



Figure 1. Plot of a molecule of  $Ru\{C \equiv CC(CN) = C(CN)_2\}$ -(PPh<sub>3</sub>)<sub>2</sub>Cp (2-Ru) (isomorphous with its Os counterpart<sup>20</sup>).



Figure 2. Plot of molecule 1 of  $Ru\{C \equiv CC(CN) = C(CN)_2\}(dppe)-Cp$  (4).

C(n)-CN bonds, which for n = 4 (1.423(2)-1.449(8) Å) are generally shorter than those to C(3) (1.443(5)-1.477(8) Å). In each case the plane containing the tricyanovinyl ligand approximately bisects the P-Ru-P angle ("vertical" orientation), although the position of the tricyanovinyl moiety with respect to the Ru defines two rotamers that can be differentiated by the Cp'(0)-Ru···C(3)-C(4) bond angle (Cp'(0) is the centroid of the Cp or Cp\* ligand), the dicyanomethylene being oriented either toward (**2-Ru**) or away (**4**, **5**) from the Cp ligand. The barrier to rotation of substitutents around the ethynyl bond in metal-ethynyl complexes is usually low, and the different ligand conformations in the present examples probably arise from packing effects rather than any significant difference in thermodynamic stability.

Comparison of the three complexes RuX(dppe)Cp\* (X =  $C \equiv CH_{2}^{27}$  C  $\equiv CC(CN) = C(CN)_{2}$  (5), and  $= C = CH_{2}^{27}$ ) (Table 2) shows significant decreases in Ru-C<sub>a</sub> (2.015(2), 1.926(6), 1.84(1) Å) and increases in the C<sub>a</sub>-C<sub>b</sub> separations



Figure 3. Plot of a molecule of  $Ru{C \equiv CC(CN) = C(CN)_2}(dppe)$ -Cp\* (5).

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	2-Ru	$3^a$	4	S	$[7]{ m BF}_4$	$[9]PF_6$	$[10] \mathrm{PF}_6^b$
			Bond Distances	(¥)			
M-P(1)	2.3211(3)	2.2947(8)	2.260(1); 2.267(1)	2.274(2)	2.3247(6)	2.283(2)	2.282(2); 2.351(2)
M-P(2)	2.3155(2)	2.3080(8)	2.263(1); 2.271(1)	2.305(2)	2.3654(6)	2.293(2)	2.299(2); 2.334(2)
M-C(cp')	2.227 - 2.288(1)	2.245-2.262(3)	2.240 - 2.261(4); 2.217 - 2.245(5)	2.254 - 2.292(5)	2.239-2.353(2)	2.223 - 2.266(8)	2.231 - 2.299(7); 2.191 - 2.229(7)
M-C(cp') (av)	2.256(27)	2.254(6)	2.249(8); 2.231(10)	2.271(16)	2.29(6)	2.243(17)	2.264(29); 2.206(15)
M-C(1)	1.920(1)	2.061(3)	1.930(3); 1.926(4)	1.926(6)	1.801(2)	$1.954(8)^{c}$	$1.909(8)^{c}$ (C(1)); $2.024(7)$ (N(1))
C(1)-C(2)	1.242(1)	1.452(4)	1.228(5); 1.224(5)	1.243(7)	1.342(3)	$1.165(11)^d$	1.24(1) (C(1))]; 1.15(1) (N(1))
C(2)-C(3)	1.378(1)	1.348(4)	1.378(5); 1.382(6)	1.388(8)	1.419(3)	1.41(1)	1.38(1); 1.43(1)
C(3)-C(4)	1.390(2)		1.391(5); 1.379(6)	1.368(8)	1.370(3)	$1.42(2)^{e}$	$1.33(1)^{e}$
C(3)-C(31)	1.443(1)	1.438(4)	1.443(5); 1.466(5)	1.477(8)	1.453(3)	1.44(1)	1.54(1); 1.41(1)
C(4)-C(41,42)	1.423, 1.425(2)	1.450, 1.448(4)	1.442, 1.424(5); 1.426, 1.428(6)	1.441, 1.449(8)	1.437, 1.431(3)		
C-N	1.151, 1.150, 1.149(2)	1.139, 1.147, 1.149, 1.140(4)	1.152, 1.140, 1.156(5); 1.133, 1.126, 1.145(5)	1.129, 1.128, 1.136(8)	1.138; 1.142, 1.145(3)	1.09(1)	1.12, 1.14(1)
			Bond Angles (di	eg)			
P(1)-M-P(2)	99.84(1)	82.60(3)	83.73(5); 83.97(5)	84.58(5)	82.78(2)	83.80(7)	83.14(8); 98.97(8)
P(1)-M-C(1)	89.98(3)	100.00(8)	86.7(1); 88.1(1)	86.0(2)	85.93(7)	90.8(2)	82.5(2); 96.4(2)
P(2)-M-C(1)	91.04(3)	88.75(7)	86.2(1); 85.7(1)	83.9(2)	88.49(7)	79.6(2)	91.2(2); 85.7(2)
M-C(1)-C(2)	169.82(8)	117.0(2)	179.5(3); 178.3(3)	174.2(5)	175.4(2)	$173.7(7)^{f}$	173.1(7) [C(1)]; 168.0(6) [N(1)]
C(1)-C(2)-C(3)	172.3(1)	124.3(3)	173.5(4); 173.5(4)	173.4(6)	126.4(2)	$174.2(10)^{g}$	176.6(9) [C(1)]; $176.2(10)$ [N(1)]
C(2)-C(3)-C(4)	124.3(1)		125.2(4); 125.2(4)	126.3(6)	124.0(2)	$119.9(11)^{h}$	125.8(9); 123.4(8)
C(2)-C(3)-C(31)	117.0(1)	120.9(2)	118.2(3); 116.5(4)	117.6(5)	117.7(2)	120.6(8)	118.8(8); 116.8(8)
C(4)-C(3)-C(31)	118.7(1)		116.6(3); 118.3(4)	116.0(5)	118.2(2)	119.5(10)	115.3(7); 119.8(8)
C(3)-C(4)-C(41,42)	118.6, 122.1(1)	123.8, 123.2(3) <sup><math>i</math></sup>	119.0, 122.4(4); 118.8, 121.8(4)	120.4, 120.7(6)	121.4, 123.4(2)		
C(41)-C(4)-C(42)	119.3(1)	113.0(3)	118.6, 119.3(4)	118.8(5)	115.2(2)		
<sup>a</sup> For 3: $C(1)-C(4) =$ Ru(1); Ru(2)/C(1);	= 1.371(4), C(3)-C(3. N(1) given as shown.	2) = 1.432(4) Å; Ru-C(1)- ${}^{c}M-C/N(1). {}^{d}C/N(1)-C($	C(4) = 127.8(2), C(2) - C(1) - C(2), C(3), JM - C/N(1) - C(3), C(3) - C/N(1) - C(3) - C/N(1) - C(3), C(3) - C/N(1) - C/N(1) - C(3) - C/N(1) -	(4) = 115.0(3), C(2) - C(2)	C(3)-C(32) = 123.3(-C(3), hC(2)-C(3), -C(3)) = 0	3), C(31)–C(3) C(3 <sup>1</sup> ). <sup>i</sup> C(1)–C	$-C(32) = 115.8(2)^{\circ}$ . <sup>b</sup> Values for (4) $-C(41,42)$ .

for

Table 2. Comparison of Some Properties of  $[RuX(dppe)-Cp^*]^{n+}$   $(n = 0, X = C \equiv CH, C \equiv CC(CN) = C(CN)_2$  (5);  $n = 1, X = C = CH_2$ )

	bond	length/Å			
compd <sup>a</sup>	Ru-C(1)	C(1)-C(2)	$\delta(C)$ (Ru-C(1))	$\delta(P)$ (dppe)	$\nu(C \equiv C) / cm^{-1}$
$[Ru^*]-C\equiv CH^b$	2.015(2)	1.202(3)	120.58	82.2	1925
5	1.926(6)	1.243(7)	215.52	80.0	1979
$[[{{Ru}^{*}_{{}_{{}_{{}_{{}_{{}_{{}_{{}_{{}_{{}_$	1.84(1)	1.29(2)	344.21	77.3	1621 <sup>c</sup>
$a[Ru^*] = Ru(dpp)$	e)Cp*. <sup>b</sup> R	leference 27	$L^{c}\nu(C=C)$		

(1.202(3), 1.243(7), 1.29(2) Å) in **5**, relative to the alkynyl complex, consistent with a resonance structure for **5** which is intermediate between the alkynyl and allenylidene tautomers of the cyanocarbon ligand, the dicyanomethylene fragment stabilizing the negative charge in the latter (Scheme 3). The

Scheme 3. Resonance Contributors to the Structure of Tricyanovinylethynyl Complexes



<sup>13</sup>C chemical shift of  $C_{\alpha}$  ( $\delta_{C}$  215.52) and the <sup>31</sup>P resonances for the dppe ligands ( $\delta_{P}$  80.0) for **5** also lie between the values found for related ethynyl and vinylidene complexes. This feature has been observed previously in one of the tcne adducts of Ru(C=CC=CFc)(dppe)Cp: namely, the tetracyanobutadienyl complex Ru{C=CC[=C(CN)\_2]CFc=C(CN)\_2}-(dppe)Cp, where Ru-C<sub> $\alpha$ </sub> = 1.915(4) Å and C<sub> $\alpha$ </sub>-C<sub> $\beta$ </sub> = 1.230(5) Å, again suggesting a significant contribution from the allenylidene tautomer Ru<sup>+</sup>{=C=C=C[C(CN)\_2^-]CFc= C(CN)\_2}(dppe)Cp.<sup>28</sup> Other spectroscopic properties are consistent with the assigned structures. In particular, the IR spectra contain unusually strong  $\nu$ (C=C) bands, the increase in intensity resulting from the strong polarization of the C=C triple bond by the electron-rich metal center (donor) and cyanocarbon (acceptor) substituents.

The tetracyanobutadienyl 3 described above has also been structurally characterized (Figure 4, Table 1). The geometries of the Ru(dppe)Cp fragment and the C[=C(CN)<sub>2</sub>]CH= C(CN)<sub>2</sub> ligand closely resemble those found for related complexes, such as Ru{C[=C(CN)<sub>2</sub>]CPh=C(CN)<sub>2</sub>}(dppe)-Cp.<sup>18</sup> In particular, the CC separations in the C<sub>4</sub> chain suggest only limited electronic delocalization, in contrast to the situation found for some other adducts of diynyl complexes, such as Ru{C≡CC[=C(CN)<sub>2</sub>]CFc=C(CN)<sub>2</sub>}(dppe)Cp mentioned above.<sup>28</sup> There is a considerable difference in the NC-C-CN angles (Table 1), and these in turn are considerably different from those in the previously considered compounds.

Spectroscopic properties of 2-Ru and 3-5 are consistent with their solid-state structures. In the IR spectra, intense



Figure 4. Plot of a molecule of  $Ru\{C[=C(CN)_2]CH=C(CN)_2\}$ -(dppe)Cp (3).

 $\nu(C\equiv\!\!=C)$  and  $\nu(CN)$  bands are found between 1975 and 1998 and between 2199 and 2213 cm<sup>-1</sup>, respectively, with broad bands at ca. 1500 cm<sup>-1</sup> arising from the C=C bond. In the <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra, the expected resonances for the Cp' and phosphine ligands are found, while in the <sup>13</sup>C NMR spectra (Table 3), three resonances for atoms of the carbon chain (C(1-3) at  $\delta$  210.71, 84.76, 118.00 for **2-Ru**) are accompanied by three CN resonances at  $\delta$  ca. 110–118. The electrospray mass spectra (ES-MS) contain strong [M + Na]<sup>+</sup> ion clusters, the Na<sup>+</sup> coming either from NaOMe added to aid ionization<sup>29</sup> or from the glass vial in which the samples were prepared for analysis.

To examine the effect of adding a second  $C \equiv C$  triple bond to the system, the reactivity of  $Ru(C \equiv CC \equiv CH)(dppe)Cp^*$ with tcne was also studied. The only product isolated from this reaction was blue  $Ru{C \equiv CC[=C(CN)_2]CH = C(CN)_2}$ -(dppe)Cp\* (6), probably formed by retro-cyclization of the initially formed [2 + 2]-cycloadduct; no evidence for displacement of a CN group was obtained. This reaction is analogous to that found for Ru(C=CC=CFc)(dppe)Cp,<sup>28</sup> although in this case only one isomer is formed. Monitoring of the <sup>31</sup>P NMR spectra of the reaction mixture showed formation of an intermediate, perhaps the [2 + 2] cycloadduct ( $\delta$  81.5), but this had disappeared after 15 min, being replaced by the signal at  $\delta$  81.4 from 6. Spectroscopic properties are consistent with addition occurring to the outer C  $\equiv$  C bond, with  $\nu$ (CN),  $\nu(C\equiv C)$ , and  $\nu(C=C)$  bands at 2209, 1964, and 1450 cm<sup>-1</sup> respectively. In the  ${}^{13}$ C NMR spectrum, resonances at  $\delta$  75.70, 88.95, 138.85, 155.90, and 222.23 arise from the carbon skeleton, the last signal being assigned to the Ru-C atom and the sixth carbon of the cyanocarbon ligand not being detected. Four CN resonances are found at  $\delta$  ca. 110–117. The ES-MS of 6 in MeCN contains  $[M + H]^+$  at m/z 813.

In MeOH, a rapid change in color of the solution of **6** from blue to orange occurs and the ES-MS shows the highest mass ion at *m*/*z* 845, corresponding to addition of (MeOH + H<sup>+</sup>) to **6**. Similar changes occurred on silica adsorbents during chromatography. Earlier related chemistry of tetracyanobutadienyls, such as W{C[=C(CN)<sub>2</sub>]CFc=C(CN)<sub>2</sub>}(CO)<sub>3</sub>Cp, which reacts with MeOH to give the orange chelate imino complex W{C[C=C(CN)(OMe)=NH}CFc=C(CN)<sub>2</sub>}-(CO)<sub>2</sub>Cp,<sup>30</sup> suggests that the orange compound formed here is Ru{C≡CC[CH=C(CN)<sub>2</sub>]=C(CN)C(OMe)=NH}-(dppe)Cp\*; similar compounds have also been isolated from reactions of  $\eta^3$ -tetracyanobutadienyl-ruthenium complexes with methoxide.<sup>19</sup>

CN	I, 4.8) 113.23, 113.65, 118.46, 122.05	113.33, 115.35, 115.96	116.03, 116.89, 117.59	5 (C= 112.38, 112.85, 113.07, 117.91	113.51, 115.40, 115.55	113.72, 116.12, 116.46	· (=CH) 110.70, 112.81, 116.79, 116.81	110.84, 112.04, 113.04	113.92, 115.22		113.69, 114.66, 115.25	112.01, 113.73, 115.62	ther resonances. <sup>b</sup> Reference 20
other C (J(CP))	76.26, 92.82, 169.57 (=CH	84.76 (C <sub>β</sub> , 2.5), 118.00 (C)	111.87, 140.21	$140.37 (=C(CN)_2), 165.25 C(CN)_2, 4)$	117.55	116.55, 138.22	75.70, 88.95, 138.85, 155.90	78.92, 113.92	102.61, 124.23, 145.61		3) 97.83, 104.42, 149.68	98.73, 102.66, 148.11	CP) or are overlapped with ot
dppe, PPh <sub>3</sub> (CH <sub>2</sub> , Ph)	128.86-135.24	$128.11 - 137.15 (PPh_3)$	128.12–137.32 (PPh <sub>3</sub> )	27.65–31.79, 128.51–135.92	28.34, 128.38-138.83	29.03-29.65, 128.04-135.55	29.21-30.47, 128.29-138.45	27.84-28.76, 127.67-133.54	28.21-29.97, 128.22-136.01	29.47-31.06, 128.22-136.01	29.43, 127.63–136.45 (dppe + PPh	29.26-29.91, 127.22-136.00	tected due to broadening from $I(t)$
Cp or $Cp^*$ (Me; ring C)	84.69 (Cp)	89.32 (Cp)	86.69 (Cp)	86.43 (Cp)	86.84 (Cp)	10.29; 97.75	10.27; 95.57	10.89; 107.67	9.82 (Ru–NC), 10.10 (Ru–CC); 93.51 (Ru–NC), 98.71 (Ru–CC)	9.54 (Os-NC), 10.13 (Ru-CC); 90.84 (Os-NC), 98.50 (Ru-CC)	84.36 (Cp); 10.23, 99.19 (Cp*)	10.10, 99.16	low-intensity <sup>13</sup> C NMR signals are unde
M−C≡ (J(CP))	192.42 m	210.71 t (22)				221.30 t (21)	222.23 m	333.20 t (19)					umber of the
formula	$^{\circ}$ Os{C[=C(CN) <sub>2</sub> ]CH=C(CN) <sub>2</sub> } (PPh <sub>3</sub> ) <sub>2</sub> CP	$Ru{C \equiv CC(CN) = C(CN)_2}{PPh_3}_2Cp$	$O_{S}(C \equiv CC(CN) = C(CN)_{2}(PPh_{3})_{2}Cp$	$Ru{C=C(CN)_{2}CH=C(CN)_{2}}$ (dppe)Cp	$Ru{C \equiv CC(CN) = C(CN)_2}(dppe)Cp$	$Ru{C \equiv CC(CN) = C(CN)_2}(dppe)Cp^*$	$Ru\{C = CC[=C(CN)_2]CH = C(CN)_2\}(dppe)Cp^*$	$[Ru{=}C{=}CHC(CN){=}C(CN)_2\} (dppe)Cp*]BF_4$	[{Cp*(dppe)Ru}{C≡CC(CN)=C(CN)CN} {Ru(dppe)Cp*}]PF <sub>6</sub>	[{Cp*(dppe)Ru}{C≡CC(CN)=C(CN)CN} {Os(dppe)Cp*}]PF <sub>6</sub>	$[\{Cp^{*}(dppe)Ru\}\{C \equiv CC(CN) = C(CN)CN\} \\ \{Ru(PPh_{3})_{2}Cp\}]PF_{6}$	$[\{Cp^{*}(dppe)Ru\}\{C \equiv CC(CN) = C(CN)CN\} \\ \{RuCl(dppe)_{2}\}]PF_{6}$	es are given in ppm (I values are given in Hz). A n
	$1-Os^{b}$	2-Ru	$2-Os^{b}$	3	4	S	6	7	8	6	10	11	<sup>a</sup> Value

#### **Organometallics**

Table 3. <sup>13</sup>C NMR Spectra of 1-Os, 2-Ru, 2-Os, and  $3-11^a$ 

Some Reactions of  $Ru{C \equiv CC(CN) = C(CN)_2}(dppe)Cp^*$ (5). The virtually quantitative formation of 5 has allowed us to study some of the chemistry of the novel ligand present in this complex. The presence of the electron-rich Ru(dppe)Cp\* and electrophilic  $=C(CN)_2$  groups confers interesting spectroscopic properties on this novel "push-pull" (donor-acceptor) complex (see below). Here we describe the protonation of 5 and the addition of other metal-ligand fragments to CN(42)(Scheme 4; see Figure 3 for atom labeling); displacement of a second CN group by other nucleophiles will be described elsewhere.31

Protonation. We were interested to examine the relative basicities of the C $\equiv$ C and C $\equiv$ N parts of the cyanocarbon ligand in 5. Addition of either  $HBF_4 \cdot OEt_2$  or aqueous  $HPF_6$  to solutions of 5 in CH<sub>2</sub>Cl<sub>2</sub> gave complex salts containing the corresponding orange vinylidene cation [Ru{C=CHC(CN)=  $C(CN)_2$  (dppe)  $Cp^*$ ]<sup>+</sup> [7]<sup>+</sup> in nearly quantitative yield. The cyanocarbon ligand structure in [7]<sup>+</sup> was readily identified from the characteristic low-field resonance for C(1), which is found at  $\delta_{\rm C}$  333.2, together with C(2) at  $\delta_{\rm C}$  113.9 and its associated proton at  $\delta_{\rm H}$  4.54. Three CN resonances are present at  $\delta_{\rm C}$  110– 113. Other signals are consistent with the ligands present on the metal center. In the IR spectrum,  $\nu(CN)$  bands are found at ca. 2216 cm<sup>-1</sup>, but no  $\nu(C \equiv C)$  band was observed. Instead, a strong band at 1612 cm<sup>-1</sup> can be assigned to  $\nu$ (C=C) arising from the vinylidene and cyanoalkene C=C bonds. The ES-MS contains a molecular cation at m/z 762, accompanied by [(M - M)]H) + Na]<sup>+</sup> at m/z 784; loss of HCN affords an ion at m/z 735. An ion at m/z 1545 corresponds to  $[(2 M - H) + Na]^+$ , perhaps formed by clustering of the cyanocarbon around the Na<sup>+</sup> center. We conclude that, in **5**, atom  $C_{\beta}$  is more basic than any of the CN groups.

A single-crystal X-ray diffraction structure determination of  $[7]BF_4$  (a plot of the cation is shown in Figure 5, and selected bond parameters are given in Table 1) has confirmed that the cationic part contains the Ru(dppe)Cp\* fragment linked to vinylidene =C=CHC(CN)=C(CN)<sub>2</sub> by a short Ru-C(1) bond (1.801(2) Å), while C(1)-C(2) has lengthened to 1.342(3) Å; C(2)-C(3) and C(3)-C(4) are 1.419(3) and 1.370(3) Å, respectively. As found for 5, C(3)-CN(31) is somewhat longer (1.453(3) Å) than C(4)-CN(41,42) (1.437, 1.431(3) Å). Other dimensions are also similar to those found in 5, although some lengthening of the Ru-C(Cp) (average 2.29(6) Å) and Ru-P bonds (2.3247, 2.3654(6) Å) has occurred as a result of reduced back-bonding from the cationic Ru center. The spread in  $Ru-C(Cp^*)$  compared with that in Ru-C(Cp) is considerable, consequent upon "tilting" of the ligand as a result of the increase in steric bulk resulting from the presence of the five Me substituents. The vinylidene and tricyanovinyl portions of the ligand are coplanar, suggesting conjugation throughout the cyanocarbon ligand, which adopts the usual horizontal position with respect to the Ru(dppe)Cp\* fragment expected of a vinylidene ligand in group 8 complexes of this type.

Addition of Metal-Ligand Fragments to CN(42) in 5. The strong donor power of the CN group to metal centers is well-known, and several groups have described the formation of polynuclear complexes using a CN group from poly-cyanometalates as a bridging ligand.<sup>32–34</sup> Other complexes are known in which an organic polynitrile bridges metal centers via CN group(s).<sup>35,36</sup> For example, several mono- or polynuclear complexes of tcne have been described, some of which exhibit unusual electronic and magnetic properties.<sup>14,37-39</sup>

Scheme 4. Addition of H<sup>+</sup> and ML<sub>n</sub> Moieties to  $Ru\{C \equiv CC(CN) = C(CN)_2\}(dppe)Cp^*$  (5)



Accordingly, we investigated the potential of the tricyanovinylethynyl group of **5** to act as a bridge between the  $Ru(dppe)Cp^*$ end cap and a second metal-ligand group.

Reactions of 5 with MCl(PP)Cp' (M = Ru, (PP)Cp' =  $(PPh_3)_2Cp$ ,  $(dppe)Cp^*$ ; M = Os,  $(PP)Cp' = (dppe)Cp^*$ ) and *cis*-RuCl<sub>2</sub>(dppe)<sub>2</sub> proceeded in refluxing MeOH in the presence of  $[NH_4]PF_6$  to give the corresponding binuclear cationic complexes  $[8]^+$ - $[11]^+$  in modest to good yields (43-68%) (Scheme 4). Three of these were fully characterized by singlecrystal X-ray diffraction studies. Plots of the cations in [9] PF<sub>6</sub> and [10]PF<sub>6</sub> are shown in Figures 6 and 7, selected bond parameters being given in Table 1; the structure of  $[8]^+$  has been previously reported.<sup>20</sup> From these structures it is clear that the cyanocarbon ligand forms an almost symmetrical bridge between the two metal centers, the second metal being attached to the CN group trans to the Ru(dppe)Cp\* group. Indeed, the similarity between the C $\equiv$ C and C $\equiv$ N groups, and the Ru/Os metal atoms in 8, despite the considerable differences in the Ru–C,N distances (>0.1 Å), results in the cations  $[8]^+$  and  $[9]^+$ being considerably/completely disordered about crystallographic inversion centers. This disadvantage is averted in  $[10]^+$  by the use of a completely different terminal component, confining the disorder to the  $C \equiv C/C \equiv N$  regions only. Other dimensions are similar to those found for 5. In the solid state, the Cp' rings in each of the bimetallic complexes  $[8]PF_{6}^{20}$ [9]PF<sub>6</sub>, and [10]PF<sub>6</sub> adopt a transoid arragement, likely a



Figure 5. Plot of the cation in  $[Ru{=C=CHC(CN)=C(CN)_2}-(dppe)Cp*]BF_4$  ([7]BF<sub>4</sub>).

consequence of packing considerations (see Computational Studies).

Spectroscopic properties of the bimetallic complexes [8–11]PF<sub>6</sub> resemble those of 5, major differences being found in the  $\nu(C\equiv C)$  bands, which shift from 1979 cm<sup>-1</sup> in 5 to ca. 1963 cm<sup>-1</sup> in the bimetallic complexes; the  $\nu(CN)$  absorptions are unaffected. In the NMR spectra of [8–10]PF<sub>6</sub>, the characteristic resonances for the Cp (or Cp\*) groups are present, while the <sup>13</sup>C resonances for the carbons of the bridging ligand are found at  $\delta_C$  ca. 98, 103, 125, and 148; the CN groups give three signals at  $\delta_C$  ca. 112–115. In the case of [11]PF<sub>6</sub>, the dppe ligands at each metal center are differentiated, with those for Ru(dppe)Cp\* at  $\delta_H$  2.35 and 2.81, while those for Ru(dppe)<sub>2</sub> occur at  $\delta_H$  2.62 and 2.81; the <sup>31</sup>P



Figure 6. Plot of the centrosymmetric cation of  $[{Cp*(dppe)Ru}_{C \equiv CC(CN)=C(CN)CN}{Os(dppe)Cp*}]PF_6$  ([9]PF<sub>6</sub>).



Figure 7. Plot of the cation of  $[{Cp*(dppe)Ru}{C \equiv CC(CN) = C(CN)CN}{Ru(PPh_3)_2Cp*}]PF_6 ([10]PF_6).$ 

resonances are at  $\delta_{\rm P}$  80.1 and 43.2, respectively. The ES-MS contain molecular cations, which fragment by successive loss of either of the metal centers; both metal-containing ions  $[\rm ML_n]^+$  are also present.

UV–Vis Absorption Spectra. The highly polarized complexes 2-Os, 2-Ru, 3–5, and [7-11]PF<sub>6</sub> are all deeply colored and show solvatochromic behavior, which led us to investigate the UV–vis spectra of representative examples (Figure 8 and Table 4). Interestingly, compound 5 did not



Figure 8. UV-vis absorption spectra: (a)  $Ru(C \equiv CH)(dppe)Cp^*$ , 3, and 6; (b) 5, [7]BF<sub>4</sub>, and [8]PF<sub>6</sub>.

Table 4. UV-Vis Absorption Maxima<sup>*a*</sup> of  $[Ru^*]C \equiv CH$ , 3, 5, 6,  $[7]BF_4$ , and  $[8]PF_6$ 

compd	$\lambda_{\rm max}/{ m nm}~(e/{ m M}^{-1}~{ m cm}^{-1})$
[Ru*]C≡CH	334 (4200)
$Ru\{C[=C(CN)_2]CH=C(CN)_2\}(dppe)Cp$ (3)	330 (10 400) (sh), 469 (3500)
$[Ru^*]{C \equiv CC(CN) = C(CN)_2} (5)$	557 (26 200)
$[Ru^*]C \equiv CC = C(CN)_2 CH = C(CN)_2 (6)$	365 (12 600), 575 (9200)
$ \begin{bmatrix} [Ru^*]C = C(H)C(CN) = C(CN)_2 \end{bmatrix} BF_4 ([7] BF_4) $	425 (28 000)
	635 (44 300)

<sup>*a*</sup>All solutions in  $CH_2Cl_2$  in fused quartz cells with a path length of 1 cm. [Ru<sup>\*</sup>] = Ru(dppe)Cp<sup>\*</sup>.

fluoresce, unlike related cyano(ethynyl)ethenes,<sup>40</sup> possibly because the metal center quenches emissions, but the associated excited-state processes were not investigated in detail.

The spectrum of Ru(C $\equiv$ CH)(dppe)Cp\* shows a relatively weak absorption band at 334 nm ( $\varepsilon$  4200 M<sup>-1</sup> cm<sup>-1</sup>) which likely has metal-to-ethynyl MLCT character. The spectrum of orange 3 (red trace) has a discernible band maximum at ca. 330 nm ( $\varepsilon$  10 400 M<sup>-1</sup> cm<sup>-1</sup>) and another broad absorption band at 469 nm ( $\varepsilon$  3500 M<sup>-1</sup> cm<sup>-1</sup>); both transitions are likely to have a degree of MLCT character associated with transitions to the ethynyl and tricyanovinyl portions of the cyanocarbon ligand. Consistent with this assignment, dark blue **6**, which features a more extensively delocalized ligand, has an absorption at 365 nm ( $\varepsilon$  12 600 M<sup>-1</sup> cm<sup>-1</sup>) and a broad band that extends into the near -IR at 575 nm ( $\varepsilon$  9200 M<sup>-1</sup> cm<sup>-1</sup>). While the spectra of complexes **3** and **6** have similar profiles, the increased conjugation in **6** results in the MLCT bands being red-shifted and having a higher molar absorption.<sup>37</sup>

Complex 5 gives rise to an intense absorption at  $\lambda_{max}$  557 nm ( $\varepsilon$  26 200 M<sup>-1</sup> cm<sup>-1</sup>) in dichloromethane, which is responsible for the characteristic purple color of this complex. This band is solvatochromic, as expected of a charge transfer transition (Figure 9 and Table 5). As the solvent polarity increases,  $\lambda_{max}$ 



Figure 9. Solvatochromism of 5 in several solvents and the formation of  $[7]^+$  upon addition of CF<sub>3</sub>CO<sub>2</sub>H.

#### Table 5. Solvatochromism of $5^a$

solvent	$\lambda_{mm}/nm$	$\varepsilon/M^{-1}$ cm <sup>-1</sup>
arr al	illax'	
$CH_2Cl_2$	557	26 200
CHCl <sub>3</sub>	557	26 500
MeCN	557	24 800
MeOH	555	26 700
acetone	554	25 700
thf	548	25 200
toluene	541	26 300
NEt <sub>3</sub>	529	24 400
CH <sub>2</sub> Cl <sub>2</sub> -hexane (1:24)	527	26 200
CH <sub>2</sub> Cl <sub>2</sub> -CF <sub>3</sub> CO <sub>2</sub> H (24:1)	425	28 000
<sup><i>a</i></sup> Solutions in fused quartz cells	with a path length of	1 cm.

shifts by ca. 30 nm (0.08 eV) along the series  $CH_2Cl_2$ -hexane (1/24) (527 nm), PhMe (541 nm),  $CH_2Cl_2$  (557 nm). This behavior results from the "push-pull" polarity conferred on the molecule by the strongly electron-donating (Ru(dppe)Cp\*) and electron-accepting (C(CN)=C(CN)\_2) substituents. Similar properties are found with organic tricyanovinyl compounds also containing electron-donating substituents, such as  $Me_2NC_6H_4C\equiv CC(CN)=C(CN)_2$ .<sup>16c,40</sup> In donor molecules with dicyanomethylene acceptor groups, this effect has been attributed to the excited state being more polar than the ground state, with the former being better stabilized in the more polar solvents.<sup>40-42</sup>

Protonation of **5** with  $CF_3CO_2H$  results in a marked blue shift of the major absorption to 425 nm ( $\varepsilon$  28 000 M<sup>-1</sup> cm<sup>-1</sup>). While in solvents such as hexane,  $CH_2Cl_2$ , and MeCN yellow [7]<sup>+</sup> persists, a shift in the position of the vinylidene/acetylide equilibrium, indicated by restoration of the purple color of **5**, occurs in  $Et_2O$ , acetone, alcohols, and  $H_2O$  even in the absence of a base, although upon concentration [7]<sup>+</sup> is regenerated. Facile deprotonation of [7]<sup>+</sup> with NEt<sub>3</sub> also regenerates **5**. This suggests the basicity/nucleophilicity of  $C_\beta$  in **5** is much lower than that in Ru(C=CH)(dppe)Cp\*, as a result of the presence of the electron-deficient cyanocarbon moiety. Addition of the second metal center in [**8**]<sup>+</sup> results in a red shift and almost doubling of the molar absorption to 635 nm ( $\varepsilon$  44 300 M<sup>-1</sup> cm<sup>-1</sup>) (Figure 8), in comparison with that of **5**. In the near-IR region, [**8**]<sup>+</sup> exhibits a weaker band at 1350 nm ( $\varepsilon$  4000 M<sup>-1</sup> cm<sup>-1</sup>).

4. Electrochemistry. The oxidative electrochemistry of  $Ru(C \equiv CR)(PP)Cp'$  complexes is characterized by the noninnocent behavior of the acetylide ligand.<sup>43,44</sup> In the present case this behavior may be expected to be moderated by the strongly electron withdrawing tricyanovinyl substituent, which should additionally offer a reductive electrochemical response. Complex 2-Ru shows two almost chemically reversible 1e processes at -0.93 and +0.97 V (in CH<sub>2</sub>Cl<sub>2</sub>/0.1 M [NBu<sub>4</sub>]PF<sub>6</sub> vs SCE, referenced to an internal decamethylferrocene/ decamethylferrocenium couple such that  $FeCp*_2/[FeCp*_2]^+ =$ -0.02 V),<sup>45</sup> and successive ligand replacement of (PPh<sub>3</sub>)<sub>2</sub>Cp with (dppe)Cp and (dppe)Cp\* gives only limited changes in redox potentials to -0.96, +1.10 V (4) and -1.00, +0.97 V (5), respectively, despite the increasing electron richness of the metal center. In the related tetracyanobutadienyl complex  $Ru\{C\}$  $C(CN)_2$ ]CH= $C(CN)_2$ }(dppe)Cp (3), two reduction events are observed (-1.29, -1.08 V), possibly arising from stepwise reduction of the two chemically distinct  $=C(CN)_2$  groups, while an anodic process gives rise to a wave at +1.05 V.

These redox processes satisfy criteria for electrochemically reversible processes, with the separation of the anodic and cathodic waves of each processes being identical with that observed for the internal decamethylferrocenium reference (ca. 70 mV),  $i_{\rm pa}/i_{\rm pc}$  ratios close to unity, and a linear relationship of peak current vs (scan rate)<sup>1/2</sup>. The bimetallic complex [8]  $PF_6$ shows three 1e events at -0.94, +0.91 and +1.30 V, the last being chemically irreversible. As with 5, these redox processes can be assigned to reduction of the tricyanovinylethynyl ligand and sequential oxidation of the metal fragment ligand at the C and N termini, albeit with a degree of  $Ru-C \equiv C$  mixing likely in the first oxidation. In further support of these assignments, it is worth noting that the simple phenylethynyl complexes Ru(C≡CPh)(PP)Cp' exhibit two redox events at +0.59 (reversible)/+1.39 (irreversible)  $(Ru(PP)Cp' = Ru(PPh_3)_2Cp)$ and +0.34 (reversible)/+1.19 V (irreversible) (Ru(PP)Cp' = Ru(dppe)Cp\*)<sup>43</sup> and [Ru(NCPh)(dppe)Cp\*]PF<sub>6</sub> exhibits an irreversible oxidation at +1.10 V,<sup>46</sup> while  $Pr_{3}^{1}SiC \equiv CC(CN) =$  $C(CN)_2$  has a single reduction process at -0.72 V associated with addition of an electron to the dicyanomethylene group to give a relatively stable anion.<sup>40</sup>

The limited variation in the redox potentials in the series of mononuclear complexes **2-Ru**, **4**, and **5** is consistent with ligand-centered redox processes in which the metal center is not appreciably involved. This suggestion is consistent with the noninnocent redox behavior of the phenylethynyl ligand in  $Ru(C \equiv CPh)(PP)Cp'$  systems.<sup>43,44</sup> The first oxidation potentials of **2-Ru**, **4**, and **5**, which are much more positive than those of the phenylethynyl systems, are also consistent with a largely

tricyanovinylethynyl ligand based oxidation. Coordination of a second metal center to the ligand in **5** results in a modestly more facile first oxidation process, consistent with the addition of an electron-donating group to the redox-active ligand, while the ligand reduction is largely unaffected. Without a broader range of compounds from which to draw comparisons, the character of the second anodic process is less clear and better addressed using spectroscopic and computational methods.

The protonated compound  $[7]^+$  does not display any oxidation events when first scanning in the anodic direction, which further supports the assignment of the first oxidation event in **2-Ru**, **4**, and **5** to an ethynyl ligand based process; oxidation of the analogous vinylidene is expected to fall at much higher potentials and probably lies outside the observable electrochemical window. However, complex  $[7]^+$  does show a chemically irreversible reduction at  $E_{pc} = -0.53$  V. Given the relative potentials of this reduction observed in the vinylidene  $[7]^+$  and the considerably more negative reduction processes associated with the dicyanomethylene portions of **2-Ru**, **4**, and **5**, reduction of  $[7]^+$  is proposed to occur on the vinylidene portion of the ligand.<sup>47</sup> Further scanning in the cathodic direction reveals a fully reversible reduction at -1.00 V, which is at the same potential as for the deprotonated compound **5**. The molecule may lose H<sup>•</sup> upon gaining an electron, generating **5**.<sup>48</sup>

#### COMPUTATIONAL STUDIES

As has been noted elsewhere, the acetylide ligand in complexes  $Ru(C \equiv CR)(PP)Cp'$  and closely related systems is redox noninnocent, being heavily involved in the oxidation processes of these complexes, and in radical cations  $[Ru(C \equiv CR)(PP)$ -Cp']<sup>+</sup> the acetylide moiety supports a substantial fraction of the unpaired electron spin density.<sup>43,44,49</sup> In the present case, the strongly electron-withdrawing nature of the tricyanovinyl substituent on the acetylide moiety renders the site of oxidation in 2-Ru, 2-Os, 4, and 5 decidedly unclear. To better understand the structural, spectroscopic, and electrochemical properties of this family of complexes, electronic structure calculations were undertaken on 5, [7]<sup>+</sup>, and [8]<sup>+</sup>, supported by UV-vis-near-IR spectroelectrochemical studies. To ensure the most reliable comparisons, full ligand sets were included in the computational model, with no symmetry constraints applied. The computational models are denoted 5',  $[7']^+$ , and  $[8']^+$  to distinguish them from the experimental systems. For both mono- and bimetallic complexes, geometry optimizations revealed a series of closely lying minima distinguished by the relative orientation of the Ru(dppe)Cp\* fragment(s) with respect to the plane of the tricyanovinylethynyl moiety, the relative energies of which were sensitive to the functional employed. The best agreement with the crystallographically determined structures was obtained with the MPW1K functional and the 3-21G\* basis set. However, the low barrier to rotation around the Ru-C(1)/N bond implied by these results indicates that the different conformations adopted by the tricyanovinylethynyl ligand in the solid-state structures of 2-Ru and 5 is likely a consequence of packing effects rather than a result of any significant electronic factors. Table 6 compares the bond lengths and angles of the crystallographically observed and optimized structures, and the good agreement of these metric parameters and of the observed and calculated IR frequencies (Table 7) give confidence in the accuracy of the computational models.

	5	5'	[7]BF <sub>4</sub>	[7']+	$[8']^+$
		Bond	Distances (Å)		
M-P(1)	2.274(2)	2.2705	2.3247(6)	2.3375	2.2888; 2.2930 <sup><i>a</i></sup>
M-P(2)	2.305(2)	2.2808	2.3654(6)	2.3179	2.2802; 2.3072 <sup><i>a</i></sup>
M-C(cp)	2.254-2.292(5)	2.243-2.306	2.239-2.353(2)	2.258 - 2.329	2.249–2.306; 2.237–2.273 <sup><i>a</i></sup>
M-C (av)	2.271(16)		2.29(6)		2.278, 2.257 <sup>a</sup>
M-C(1)	1.926(6)	1.944	1.801(2)	1.825	1.919 (C(1)); 2.048 $(N(1))^a$
C(1) - C(2)	1.243(7)	1.233	1.342(3)	1.325	1.243 (C(1)); 1.160 $(N(42))^a$
C(2) - C(3)	1.388(8)	1.378	1.419(3)	1.439	1.360
C(3) - C(4)	1.368(8)	1.376	1.370(3)	1.362	1.395
C(3)-C(31)	1.477(8)	1.427	1.453(3)	1.418	1.428
C(4) - C(41, 42)	1.441, 1.449(8)	1.406, 1.407	1.437, 1.431(3)	1.413, 1.411	1.403; 1.396
C-N	1.152, 1.128, 1.136(8)	1.155, 1.158, 1.158	1.138; 1.142, 1.145(3)	1.155, 1.156, 1.157	1.159; 1.156
		Bond	l Angles (deg)		
P(1)-M-P(2)	84.58(5)	83.38	82.78(2)	82.49	82.23; 83.09 <sup><i>a</i></sup>
P(1)-M-C(1)	86.0(2)	83.43	85.93(7)	96.64	90.23; 84.29 <sup><i>a</i></sup>
P(2)-M-C(1)	83.9(2)	90.35	88.49(7)	83.61	83.03; 91.62 <sup><i>a</i></sup>
M-C(1)-C(2)	174.2(5)	173.42	175.4(2)	166.7	175.94 (C(1)); 173.47 (N(42))
C(1)-C(2)-C(3)	173.4(6)	176.4	126.4(2)	128.9	176.88 (C(1)); 178.80 (N(42))
C(2)-C(3)-C(4)	126.3(6)	124.4	124.0(2)	121.9	125.1
C(2)-C(3)-C(31)	117.6(5)	116.6	117.7(2)	119.0	117.2
C(4)-C(3)-C(31)	116.0(5)	119.09	118.2(2)	118.9	118.7
C(3)-C(4)-C(41,42)	120.4, 120.7(6)	118.4, 122.4	121.4, 123.4(2)	119.6, 122.0	119.3, 121.9
<sup><i>a</i></sup> Equivalent data from I	Ru(2).				

contexts from calculations at various different levels of theory on several previous occasions.<sup>43,44,50–52</sup> A qualitative analysis of the pseudo-octahedral [RuC $\equiv$ CR(L<sub>2</sub>)Cp'] fragment reveals a lifting of the degeneracy of the t<sub>2g</sub> type orbitals by interactions with the Cp' ligand. Of this set, two are of the correct symmetry to interact with the  $\pi$  orbitals of the alkynyl ligand, and in the case of **5**' the antibonding combinations of these d $\pi$  orbitals feature in the HOMO and HOMO-2. Furthermore, the orthogonal nature of these orbital fragments results in different degrees of spatial distribution of the HOMO and HOMO-2 over the Ru{C $\equiv$ CC=(CN)C(CN)<sub>2</sub>} backbone (Table 8), with greater participation of the cyanocarbon fragment in the HOMO than in the HOMO-2 (Figure 10). The HOMO-1 is derived from the third orbital of the t<sub>2g</sub>-like set and is more localized on the Ru(dppe)Cp\* fragment.

The LUMO of 5' is well removed from the HOMO  $(|\Delta E_{\text{HOMO-LUMO}}| = 4.3 \text{ eV})$  and other unoccupied (metal- and phosphine-based) orbitals and essentially comprises the C  $\equiv$  CC(CN)=C(CN)<sub>2</sub>  $\pi^*$  system, with a limited contribution from

Table 7. Selected Observed  $(CH_2Cl_2/cm^{-1})$  and Calculated (vacuum/cm<sup>-1</sup> with Oscillator Strength Given in Parentheses)<sup>*a*</sup> IR Bands in 5, [7]<sup>+</sup>, and [8]<sup>+</sup> (as the [PF<sub>6</sub>]<sup>-</sup> Salts) and from the Optimized Geometries of 5', [7']<sup>+</sup>, and [8']<sup>+</sup>

	$\nu(C \equiv C)$	$\nu(C=C)$	$ u(\mathrm{CN}) $
5	1979 vs	1463 s	2209 m; 2199 w
5'	2024 (2579)	1450 (454)	2242 (6); 2230 (55); 2216 (26)
$[7]PF_6$	1612 s	1612 s	2216 m
[7']+	$1588 (1234)^b$	1503 (111)	2252 (27); 2243 (2); 2236 (10)
[8]PF <sub>6</sub>	1963 vs	1448 s	2209 w
<b>[8</b> '] <sup>+</sup>	1984 (5878)	1400 (846)	2233 (10); 2215 (82); 2193 (45)
<sup>a</sup> At the M	ADW1K/3-21C	* lovel with a	frequency correction of $0.92^{-49c}$

<sup>*a*</sup>At the MPW1K/3-21G<sup>\*</sup> level with a frequency correction of 0.92.<sup>49c</sup>  ${}^{b}\nu$ (C=CHC).

the metal fragment (Table C1). The partial spatial overlap of the HOMO and LUMO permits a facile HOMO–LUMO optical transition with a degree of MLCT character. Indeed, the solvatochromic absorption band observed in the solution-phase spectra of **5** between 527 and 557 nm (Table 5) is reproduced by TD DFT calculations from **5**' as the HOMO–LUMO transition, which is found at 409 nm in the gas-phase calculations.

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The computational model of the vinylidene  $[7']^+$  reproduced the crystallographically observed 'horizontal' ligand conformation, with the  $C(4)-C(3)\cdots Ru-C(0)$  angle in the optimized structure of  $[7']^+$  calculated to be  $-81.37^\circ$ . An examination of the frontier orbital composition (Table 9, Figure 11) reveals that the vinylidene ligand serves to decouple the metal fragment from the tricyanovinyl moiety in the HOMO. The LUMO retains considerable tricyanovinyl character, while the vinylidene ligand contributes strongly to the LUMO+1, which is only some +0.73 eV higher in energy than the LUMO, and the LUMO+2 is strongly metal in character and  $\delta$  symmetry with respect to the vinylidene ligand; the relative order of these orbitals may be sensitive to the level of theory employed, and we note that reorganization of the orbital manifold may take place upon reduction; for comparison, the LUMOs of monoand dicyanovinylidene complexes of the Ru(dppe)Cp\* moiety are weighted heavily on  $C_a$ .<sup>46</sup> The HOMO-2 has  $\pi$  character and is extensively delocalized over the C=C(H)-C(CN)=C(CN)<sub>2</sub> portion of the molecule. The nodes between Ru-C(1) and C(2)-C(3) are consistent with the valence bond description of the ligand. In the case of  $[7']^+$ , TD DFT calculations indicate that the lowest energy electronic transition has HOMO–LUMO (MLCT) character but that this transition is blue-shifted (349 nm) with respect to the analogous MLCT transition in 5', in good agreement with the observed spectra (Figure 8b).

The bimetallic complex model  $[8']^+$  gave rise to a series of closely lying minima with the cisoid conformer lying only

#### Table 8. Energy (eV) and Composition (%) of Selected Frontier Orbitals in 5' (MPW1K/3-21G\*)

					compos	ition			
МО	energy	Ru	Cp*	dppe	C1≡C2	C3=C4	CN31	CN41	CN42
201 LUMO+4	-0.02	4	2	93	0	0	0	0	0
200 LUMO+3	-0.07	4	1	94	0	0	0	0	0
199 LUMO+2	-0.30	4	2	94	0	0	0	0	0
198 LUMO+1	-0.41	15	9	76	0	0	0	0	0
197 LUMO	-1.92	5	1	2	16	45	14	10	8
196 HOMO	-6.22	30	19	11	18	13	0	4	5
195 HOMO-1	-6.49	37	42	14	7	0	0	0	0
194 HOMO-2	-7.27	36	18	7	34	2	1	0	1
193 HOMO-3	-7.35	12	37	23	15	8	1	2	3
192 HOMO-4	-7.97	42	12	46	1	0	0	0	0
191 HOMO-5	-8.16	9	3	84	1	1	0	1	1





HOMO-2

HOMO-1

Figure 10. Plots of selected frontier orbitals from 5' (isocontour value  $\pm 0.04$  (e/bohr<sup>3</sup>)<sup>1/2</sup>).

Гable 9. Energy (eV) a	nd Composition (%	) of Selected Frontier	Orbitals in $[7']$	+ (MPW1K/3-21G*)
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					composi	tion			
МО	energy	Ru	Cp*	dppe	C1=C2H	C3=C4	CN31	CN41	CN42
201 LUMO+4	-2.88	11	6	78	4	0	0	0	0
200 LUMO+3	-3.06	12	6	80	2	0	0	0	0
199 LUMO+2	-3.53	30	21	49	0	0	0	0	0
198 LUMO+1	-4.30	26	7	7	52	5	1	1	1
197 LUMO	-5.03	5	1	1	15	47	13	10	8
196 HOMO	-9.91	29	43	12	11	3	0	1	1
195 HOMO-1	-10.07	10	42	30	12	4	0	1	2
194 HOMO-2	-10.27	15	20	19	21	14	1	4	6
193 HOMO-3	-10.65	1	2	96	0	0	0	0	0
192 HOMO-4	-10.84	1	1	97	0	0	0	0	0
191 HOMO-5	-10.86	6	3	90	1	0	0	0	0

+7.5 kJ mol<sup>-1</sup> higher than the transoid structure, the transoid conformer being the more closely related to the crystallographically observed structure. The energies and composition of selected frontier orbitals from the transoid conformer of  $[8']^+$ , summarized in Table 10 and illustrated in Figure 12, are well described in terms of the addition of a  $[Ru(dppe)Cp^*]^+$  fragment to the metallo ligand 5', with limited mixing of the orbital character of the two fragments (Table 10).



HOMO-2

HOMO-1

Figure 11. Plots of selected frontier orbitals from  $[7']^+$  (isocontour value  $\pm 0.04$  (e/bohr<sup>3</sup>)<sup>1/2</sup>), with hydrogen atoms omitted for clarity.

Гable 10. Energy	r (eV) :	and Compos	ition (%)	of Selected	Frontier	Orbitals in	[8']+	(MPW1K/3-21G*)	)
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						compo	sition					
МО	energy	Ru1	Cp-1	dppe-1	C1≡C2	C3=C4	CN31	CN41	CN42	Ru2	Cp-2	dppe-2
365 LUMO+4	-1.90	0	0	1	0	0	0	0	1	6	3	87
364 LUMO+3	-1.96	0	0	0	0	0	0	0	0	7	4	88
363 LUMO+2	-2.03	18	12	69	0	0	0	0	0	0	0	1
362 LUMO+1	-2.15	0	0	0	0	0	0	0	0	19	10	70
361 LUMO	-4.11	9	2	2	19	38	14	6	8	1	0	0
360 HOMO	-7.90	22	17	10	12	12	0	4	5	11	5	3
359 HOMO-1	-8.25	32	48	14	6	0	0	0	0	0	0	0
358 HOMO-2	-8.39	4	8	4	1	2	0	0	4	26	31	19
357 HOMO-3	-8.66	0	1	1	0	0	0	0	2	43	37	15
356 HOMO-4	-9.05	41	13	6	33	2	2	0	0	1	1	0
355 HOMO-5	-9.06	11	28	20	12	7	0	2	3	6	6	4

The Ru(dppe)Cp\* fragment orbitals from the N ligand moiety interleave with the orbitals derived from 5' in the frontier region and comprise the HOMO-3, HOMO-2, and LUMO+1 in the bimetallic system  $[8']^+$ . The HOMO–LUMO gap in  $[8']^+$  ( $|\Delta E_{\text{HOMO-LUMO}}| = 3.79 \text{ eV}$ ) is somewhat smaller than in 5 as a result of the stabilization of the LUMO by the cationic charge, and

consequently the HOMO–LUMO transition in the bimetallic complex is red-shifted relative to the mononuclear precursor.

### DISCUSSION

Over 20 years ago, the formal [2 + 2]-cycloaddition of tetracyanoethene to  $\sigma$ -alkynyl-transition-metal complexes to



HOMO-3

HOMO-2

Figure 12. Plots of selected frontier orbitals from  $[8']^+$  (isocontour value  $\pm 0.04$  (e/bohr<sup>3</sup>)<sup>1/2</sup>), with hydrogen atoms omitted for clarity.

give labile tetracyanocyclobutenyl–metal derivatives, followed by their retro-electrocyclic ring opening to the corresponding tetracyanobutadienyl–metal complexes, was described.<sup>17,18</sup> In the intervening years, similar reactions have been described with several other electron-deficient alkenes, such as  $(CF_3)_2C=C(CN)_2$ ,  $R^1CH=CR^2(CN)$  ( $R^1 = Ph$ ,  $C_6H_4NO_2$ -4;  $R^2 = CN$ ,  $CO_2Et$ ,  $C_6H_4NO_2$ -4), and  $(MeO_2C)CH=$  $C(CN)(CO_2Me)$ .<sup>30,53</sup> In several cases, the intermediate cyclobutenyls were not isolated or even observed. More recently, similar reactions of purely organic alkynes have been studied, first by Hopf and co-workers<sup>15</sup> and later by Diederich and his group.<sup>16</sup> The latter group has recently extended these studies to the addition of 2,2-dicyanovinylalkenes to alkynes containing donor substituents.<sup>40</sup>

The present work arose out of an attempt to obtain similar tetracyanobutadienyl derivatives from the parent ethynyl–ruthenium complexes,  $Ru(C \equiv CH)(PP)Cp'$  ((PP)Cp' = (PPh<sub>3</sub>)<sub>2</sub>Cp, (dppe)Cp, (dppe)Cp\*). We were surprised to find that instead of the well-established [2 + 2]-cyclo-addition reaction, displacement of a CN group from the cyanoalkene by

the ethynyl-metal group had occurred. The alkynyl complexes were thus acting as significant nucleophiles, attacking at an olefinic carbon, with elimination of HCN. In this, the chemistry resembled much more the characteristic chemistry of tcne with more conventional nucleophiles, such as alcohols, thiols and amines, which had been detailed in the early studies of the du Pont group.<sup>2</sup> Substitution of tcne by alkynyllithiums or -coppers has been described.<sup>40,54,55</sup>

The formation of the tricyanovinylethynyl complexes described above results from the strong steric protection afforded to the ethynyl groups in the precursors, the metal—ligand fragment becoming more bulky along the series Ru(dppe)Cp < Ru-(PPh<sub>3</sub>)<sub>2</sub>Cp < Ru(dppe)Cp\*. In addition, the electronic changes on proceeding along this series cannot be discounted, Cp\* being more basic (a stronger electron donor) than Cp. We recall a similar effect upon the reactions of MeOH with the related vinylidenes [Ru(=C=CH<sub>2</sub>)(PP)Cp']<sup>+</sup>, where rapid attack on  $C_{\alpha}$  to give the corresponding carbenes [Ru{CMe(OMe)}-(PP)Cp']<sup>+</sup> occurs with (PP)Cp' = (PPh<sub>3</sub>)<sub>2</sub>Cp, (dppe)Cp, but the (dppe)Cp\* complex is unreactive (cf. the synthesis of Ru(C≡CH)(dppe)Cp\* described below). Space-filling models of the ethynyl complexes also show that C<sub>α</sub> is well shielded by the (PP)Cp' ligands, particularly in Ru(C≡CH)(dppe)Cp\*, while C<sub>β</sub> is slightly exposed, allowing it to attack the olefinic carbon of tcne.

There are several examples of the replacement of one or more CN groups of tcne in its reactions with organometallic compounds. At high temperatures in polar solvents, ferrocene reacts with tcne to give a mixture of FcCN and FcC(CN)= $C(CN)_2^{56,57}$  while TlCp gives Tl{ $C_5H_4C(CN)=C(CN)_2$ }.<sup>58</sup> Similar reactions have been observed with the Ir(CH<sub>2</sub>CMe<sub>2</sub>- $C_6H_4$ )( $C_6H_4Bu^t$ -2)( $Bu^t_2$ -bpy) complex, where substitution occurred on the aryl ring to give Ir{ $CH_2CMe_2C_6H_3$ [C-(CN)= $C(CN)_2$ ]-4}( $C_6H_4Bu^t$ -2)( $Bu^t_2$ -bpy),<sup>59</sup> while the formation of cyano complexes indicates similar reactions occur with [*fac*-Re(CO)<sub>3</sub>(bpy)MeOH)]<sup>+ 60</sup> and {Fe(CO)<sub>2</sub>Cp}<sub>2</sub>.<sup>61</sup>

The monometallic tricyanovinylethynyl (1,1,2-tricyanobut-1en-3-yn-4-yl) complexes described herein are deep purple solids, which crystallize readily and were originally characterized by single-crystal X-ray diffraction structure determinations, supported by elemental microanalyses and mass spectrometric studies. Their IR and NMR spectra contain absorptions or resonances characteristic of the C $\equiv$ C triple bond and C $\equiv$ N groups, as well as of the M(PP)Cp' (M = Ru, Os) fragments. In the <sup>13</sup>C NMR spectra, only three resonances between  $\delta$  114 and 120 are found for the CN groups, in contrast to the four signals usually obtained for the tetracyanobutadienyl complexes. In the <sup>31</sup>P NMR spectra, the tricyanovinylethynyl complexes give singlet resonances, while the phosphine ligand resonances are found as AB quartets for the  $\eta^1$ -tetracyanobutadienyls, as a result of the asymmetry of the cyanocarbon ligand. The observation of different conformations of the tricyanovinylethynyl ligand (being "up" or "down" with respect to the Cp' ligand) in the crystallographically determined structures of 2-Ru, 4, and 5 is consistent with the flat potential energy surface associated with ligand rotation determined by DFT calculations.

The presence of the tricyanovinyl substituent significantly alters the electronic structure of the complexes  $M{C \equiv}$  $CC(CN) = C(CN)_2 (PP)Cp'$  relative to the phenylacetylide analogues M(C≡CPh)(PP)Cp'. The low-lying cyanocarbon  $\pi^*$  system which comprises the LUMO of these systems has appreciable special overlap with the HOMO, which is largely associated with the  $M-C\equiv C$  portion of the molecule. This effective overlap leads to an intense, solvatochromic MLCT band that in turn gives rise to the characteristic purple color of these donor-acceptor ("push-pull") complexes. Some electrochemical studies have been carried out, which incorporate comparative studies with analogous cyanocarbon derivatives. The tricyanovinylethynyl complexes are reduced at much less negative potentials (ca. -1.0 V vs SCE) than the phenylacetylide derivatives, for which reduction is not usually observed within the normal solvent window, and reduction likely is associated with the population of the cyanocarbon ligand based LUMO. The complexes also exhibit an oxidation process at ca. +0.9 V which is more closely associated with oxidation of the C-ligated ruthenium center and  $C \equiv C$  group. The much more positive potential of this oxidation relative to that of the phenylacetylide examples is consistent with the strongly electron withdrawing nature of the tricyanovinyl moiety.

Addition of the proton to the ethynyl  $C_{\beta}$  is notable and suggests that  $C_{\beta}$  is more electron rich than the N atoms of the CN groups. Protonation of **5** to give vinylidene [7]<sup>+</sup> results in a

significant increase in the energy of the MLCT transition with concomitant change in the color of the solution to yellow. The vinylidene ligand adopts the usual "horizontal" orientation in the solid state. In contrast, however, a second  $ML_n$  fragment (here we have used M'(PP)Cp' (M' = Ru, (PP)Cp' =  $(PPh_3)_2Cp$ ,  $(dppe)Cp, (dppe)Cp^*; M' = Os, (PP)Cp' = (dppe)Cp')$  and *trans*-[RuCl(dppe)<sub>2</sub>] adds to the CN group trans to the  $-C \equiv C$ -Ru(dppe)Cp\* group. Steric effects may dictate this result, a second bulky  $ML_n$  fragment not being able to add to  $C_{\alpha}$ although four Fp moieties (less bulky than the Ru(dppe)Cp\* group employed here) are found N-bonded to tcne in  $[{Fe(CO)_2Cp}_4(\mu_4-tcne)]^{n+}$  (n = 3, 4).<sup>7</sup> These monocations have the expected solid-state structures, although the similarity between  $C \equiv C$  and  $C \equiv N$  results in disorder in the structures of 8 and 9, making these two groups experimentally indistinguishable. DFT studies, supported by the electrochemical results, suggest that there is only limited delocalization between the two metal centers in 8, with the HOMO and HOMO-1 being localized on the C-ligated metal atom and the HOMO-2 and HOMO-3 being more closely associated with the N-ligated metal center.

#### CONCLUSIONS

This work has demonstrated the ready displacement of one of the CN groups of tcne by ethynyl-ruthenium or -osmium groups, which behave as strong nucleophiles akin to alkoxide, thiolate, or amines. The resulting tricyanovinylethynyl complexes are novel examples of donor-acceptor molecular arrays and show the expected solvatochromism. Addition of a second metal-ligand fragment to a CN group trans to the metal center has given further examples of binuclear complexes containing carbon-rich polynitriles as bridging groups.

The chemistry of tcne contains many examples of the replacement of a second CN group on the same carbon atom (gem disubstitution), these reactions being driven by the excellent leaving properties of the CN group(s) and the stabilization of the negative charge on the  $=C(CN)_2$  group.<sup>3,4</sup> Disubstitution by a second  $-C \equiv CRu(PP)Cp'$  group is not found in the present study, no doubt because of the strong steric interactions which would occur if two such ML<sub>n</sub> groups were on the same carbon atom. However, as we have briefly reported,<sup>20</sup> the use of smaller nucleophiles has indeed resulted in the formation of a range of dicyanoethene derivatives, which will be described in detail elsewhere.<sup>31</sup>

#### 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), or by flash chromatography on silica gel (Davisil 40–63  $\mu$ m).

**Instrumentation.** IR spectra were obtained using a Bruker IFS28 FT-IR spectrometer. Spectra in  $CH_2Cl_2$  were obtained using a 0.5 mm path length solution cell with NaCl windows. Nujol mull spectra were obtained from samples mounted between NaCl disks. UV–vis–near-IR spectra were obtained with a Varian Cary 5000 spectrometer: sample solutions were in fused quartz cells, path length 1 cm. NMR spectra were recorded on a Varian Gemini 2000 instrument (<sup>1</sup>H at 300.145 MHz, <sup>13</sup>C at 75.479 MHz, <sup>19</sup>F at 282.388 MHz, <sup>31</sup>P at 121.501 MHz) or Varian Unity Inova 600 instrument equipped with a cryoprobe (<sup>1</sup>H at 599.653 MHz, <sup>13</sup>C at 150.796 MHz). Unless otherwise stated, samples were dissolved in CDCl<sub>3</sub> contained in 5 mm sample tubes. Chemical

shifts are given in ppm relative to internal tetramethylsilane for <sup>1</sup>H and <sup>13</sup>C NMR spectra and external  $H_3PO_4$  for <sup>31</sup>P NMR spectra. Unless otherwise stated, electrospray (ES-MS) or high-resolution (HR-MS) mass spectra were obtained from samples dissolved in MeOH which contained NaOMe as an aid to ionization.<sup>29</sup> Solutions were injected into a Finnegan LCG (ES-MS, Adelaide) or Bruker MicrOTOF (HR-MS, Waikato) spectrometer via a 10 mL injection loop. Nitrogen was used as the drying and nebulizing gas. Peaks listed are the most intense of the isotopic clusters. Elemental analyses were by the CMAS, Belmont, Victoria 3216, Australia, and Campbell Microanalytical Centre, University of Otago, Dunedin, New Zealand.

**Reagents.** The compounds RuCl(dppe)Cp<sup>\*</sup>,<sup>62</sup> RuCl(PPh<sub>3</sub>)<sub>2</sub>Cp,<sup>63</sup> Ru(C≡CH)(PPh<sub>3</sub>)<sub>2</sub>Cp,<sup>64</sup> Ru(C≡CC≡CH)(dppe)Cp<sup>\*</sup>,<sup>65</sup> [M(= C=CH<sub>2</sub>)(dppe)Cp']PF<sub>6</sub> (Cp' = Cp, Cp\*; M = Ru,<sup>27</sup> Os<sup>50b</sup>), *cis*-RuCl<sub>2</sub>(dppe)<sub>2</sub>,<sup>66</sup> and HC≡CSiMe<sub>3</sub><sup>67</sup> were all prepared by the cited literature procedures. Os(C≡CH)(PPh<sub>3</sub>)<sub>2</sub>Cp was prepared by deprotonation of [Os(=C=CH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>Cp]PF<sub>6</sub> with KOBu<sup>t.68</sup> All other reagents were obtained from Sigma-Aldrich or Fluka and used as received without further purification.

**Ru(C=CH)(dppe)Cp\*.** A degassed solution of  $Me_3SiC=CH$ (2.1 mL, 14.90 mmol) in MeOH (20 mL) was added to a mixture of RuCl(dppe)Cp\* (2.0 g, 2.98 mmmol) and  $[NH_4]PF_6$  (0.971 g, 5.96 mmol) in a Schlenk flask. The mixture was heated to reflux for 2 h and cooled to room temperature, and then sodium metal (0.343 g, 14.90 mmol) was added to give a yellow precipitate. After 1 h, this was collected and washed with MeOH (2 × 5 mL) and hexane (5 mL) to give Ru(C=CH)(dppe)Cp\* as a yellow powder (1.91 g, 95%).

**Reactions of Ethynyl or Vinylidene Complexes with tcne.** *Caution*! Extremely toxic HCN is produced in these reactions! Appropriate care should be taken, working in a well-ventilated area. HCN and accompanying solvent were collected in a trap cooled in liquid  $N_2$ . After it was warmed to room temperature, the condensate was treated with KMnO<sub>4</sub> solution.

 $Ru(C \equiv CH)(PPh_3)_2Cp$ . To a solution of  $Ru(C \equiv CH)(PPh_3)_2Cp$  (70 mg, 0.098 mmol) in thf (12 mL) was added tcne (13 mg, 0.102 mmol). The color of the solution changed from yellow to yellow-brown to red to burgundy over a 30 min period. After 2 h, no further color change was observed and solvent was removed. The residue was purified by preparative TLC (acetone-hexane, 3:7) affording two bands.

Extraction of the lower red band ( $R_f = 0.4$ ) gave Ru{C[= C(CN)\_2]CH=C(CN)\_2}(PPh<sub>3</sub>)<sub>2</sub>Cp (1-Ru; 53 mg, 64%). Anal. Calcd ( $C_{49}H_{36}N_4P_2$ Ru): C, 69.74; H, 4.30; N, 6.64; *M*, 844. Found: C, 68.83; H, 4.54; N, 6.47. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>):  $\nu$ (C=N) 2226 w, 2207 m,  $\nu$ (C=C) 1605 m, 1480 m, 1433 s, 1414 w. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  4.78 (s, 5H, Cp), 5.90 (s, 1H, C=CH), 7.10–7.49 (m, 30 H, Ph). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  45.2, 42.2 (AB q, *J*(PP) = 33 Hz, 2P, Ru(PPh<sub>3</sub>)<sub>2</sub>). ES-MS (*m*/*z*): 867, [M + Na]<sup>+</sup>.

The upper purple band ( $R_f = 0.6$ ) contained  $Ru\{C \equiv CC(CN) = C(CN)_2\}(PPh_3)_2Cp$  (2-**Ru**; 8 mg, 10%) as a dark purple solid. X-rayquality crystals were grown from  $CDCl_3/MeOH$ . Anal. Calcd ( $C_{48}H_{35}N_3P_2Ru \cdot CDCl_3$ ): C, 62.86; H, 3.88; N, 4.49; *M*, 817. Found: C, 62.98; H, 3.93; N, 4.44. IR ( $CH_2Cl_2$ , cm<sup>-1</sup>):  $\nu(C \equiv N)$ 2213 w, 2204 w,  $\nu(C \equiv C)$  1991 vs,  $\nu(C = C)$  1605 m, 1481 m, 1462 s, 1434 m. <sup>1</sup>H NMR ( $CDCl_3$ ):  $\delta$  4.62 (s, 5H, Cp) 7.16–7.30 (m, 30 H, Ph). <sup>13</sup>C NMR ( $CDCl_3$ ):  $\delta$  84.76 (t, J(CP) = 2.5 Hz,  $C_{\beta}$ ), 89.32 (s, Cp), 113.33, 115.35, 115.96 (3s, CN), 118.00 (s, C), 128.11–137.15 (Ph), 210.71 (t, J(CP) = 22 Hz,  $C_{\alpha}$ ); in  $C_6D_{6^{j}} \delta$  77.73 (t, J = 32 Hz, CDCl<sub>3</sub>). <sup>31</sup>P NMR ( $CDCl_3$ ):  $\delta$  48.6 (s, 2P, Ru(PPh\_3)\_2). ES-MS (m/z): 840, [M + Na]<sup>+</sup>.

 $Ru(=C=CH_2)(PPh_3)_2Cp/LiBu$ . A solution of  $[Ru(=C=CH_2)-(PPh_3)_2Cp]PF_6$  (175 mg, 0.20 mmol) in thf (15 mL) at -78 °C was treated with LiBu (0.23 mL of a 1.8 M solution in hexane, 0.41 mmol). After 30 min, tcne (52 mg, 0.41 mmol) was added to the reaction mixture and was warmed to room temperature. The color changed from yellow to dark purple, and after 2 h hexane (15 mL) was added and the mixture was passed through a small column (silica, acetone-petroleum spirit, 3:7). Further purification by flash chromatography (silica, CH<sub>2</sub>Cl<sub>2</sub>-hexane, 3:1) gave 2-Ru as a purple solid (61 mg, 37%).

 $Os(C \equiv CH)(PPh_3)_2Cp$ . A reaction similar to that for Ru(C  $\equiv$  CH)(PPh\_3)\_2Cp, using Os(C  $\equiv$  CH)(PPh\_3)\_2Cp (32 mg, 0.04 mmol) and tcne (6 mg, 0.044 mmol), gave the following products.

Os{C[=C(CN)<sub>2</sub>]CH=C(CN)<sub>2</sub>}(PPh<sub>3</sub>)<sub>2</sub>Cp (1-Os; 11 mg, 30%) ( $R_f$  = 0.4) was obtained as a dark red solid. X-ray-quality crystals were grown from C<sub>6</sub>H<sub>6</sub>/MeOH. Anal. Calcd (C<sub>49</sub>H<sub>36</sub>N<sub>4</sub>OsP<sub>2</sub>): C, 63.08; H, 3.89; N, 6.00; *M*, 934. Found: C, 62.56; H, 3.86; N, 5.91. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>):  $\nu$ (C≡N) 2228 w, 2204 m,  $\nu$ (C=C) 1605 w, 1480 m, 1435 s, 1414 w. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  4.98 (s, 5H, Cp), 5.82 (s, 1H, C=CH), 7.05–7.45 (m, 30 H, Ph). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  76.26, 92.82 (s, C), 84.69 (s, Cp), 113.23, 113.65, 118.46, 122.05 (4s, CN), 128.86– 135.24 (m, Ph), 169.57 (d, *J*(CP) = 4.8 Hz, =CH), 192.42 (m, Os– C<sub>a</sub>). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  −0.1, −5.2 (AB q, *J*(PP) = 17 Hz, 2P, Os(PPh<sub>3</sub>)<sub>2</sub>). ES-MS (*m*/*z*): 1889, [2 M + Na]<sup>+</sup>; 957, [M + Na]<sup>+</sup>; 935, [M + H]<sup>+</sup>; 781, [Os(PPh<sub>3</sub>)<sub>2</sub>Cp]<sup>+</sup>.

Os{C≡CC(CN)=C(CN)<sub>2</sub>}(PPh<sub>3</sub>)<sub>2</sub>Cp (2-Os; 8 mg, 22%) ( $R_f = 0.5$ ) was obtained as a dark purple solid. X-ray-quality crystals were grown from CH<sub>2</sub>Cl<sub>2</sub>/hexane. Anal. Calcd (C<sub>48</sub>H<sub>35</sub>N<sub>3</sub>OsP<sub>2</sub>): C, 63.65; H, 3.89; N, 4.64; M, 907. Found: C, 63.90; H, 3.90; N, 4.62. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>):  $\nu$ (C≡N) 2210 w,  $\nu$ (C≡C) 1998 (sh), 1975 vs,  $\nu$ (C=C) 1481 w, 1457 m, 1435 w. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  4.78 (s, 5H, Cp) 7.14–7.28 (m, 30 H, Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  86.69 (s, Cp), 111.87, 140.21 (2s, C), 116.03, 116.89, 117.59 (3s, CN) 128.12–137.32 (Ph). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  2.8 (s, 2P, Os(PPh<sub>3</sub>)<sub>2</sub>). ES-MS (m/z): 930, [M + Na]<sup>+</sup>.

 $Ru(C \equiv CH)(dppe)Cp$ . To a stirred thf solution (10 mL) of Ru(C  $\equiv$ CH)(dppe)Cp (57 mg, 0.097 mmol) in thf (10 mL) was added tcne (14 mg, 0.106 mmol). The solution slowly turned from yellow to transparent dark red and then to orange after 5 h. The reaction was monitored by spot TLC: the initial upper burgundy band was replaced by an orange band. After 7 h, solvent was removed and the residue was purified by column chromatography (flash silica, acetone-petroleum spirit, 3:7). An orange fraction contained Ru{C[=C(CN)<sub>2</sub>]CH= C(CN)<sub>2</sub>]}(dppe)Cp (3) as an orange solid (55 mg, 79%). X-rayquality crystals were grown from CH2Cl2-hexane. Anal. Calcd  $(C_{39}H_{30}N_4P_2Ru)$ : C, 65.27; H, 4.21; N, 7.81; *M*, 718. Found: C, 65.30; H, 4.25; N, 7.78. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>):  $\nu$ (C=N) 2228 m, 2213 s,  $\nu$ (C=C) 1605 m, 1556 m. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.36, 2.80 (2m, 2 × CH<sub>2</sub>, dppe), 4.94 (s, 5H, Cp), 6.76 (s, 1H, C=CH), 6.83-7.69 (m, Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 27.65-31.79 (m, PCH<sub>2</sub>CH<sub>2</sub>P), 86.43 (s, Cp), 112.38, 112.85, 113.07, 117.91 (4s, CN), 128.51-135.92 (m, Ph), 140.37 (s, C= $C(CN)_2$ ), 165.25 (d, J(CP) = 4 Hz, C= $C(CN)_2$ ). <sup>31</sup>P NMR (CDCl<sub>3</sub>): at room temperature,  $\delta$  82.3 (br s, P, Ru(dppe)), 72.6 (vbr s, P, Ru(dppe)); at -57 °C,  $\delta$  80.8 (d, J(PP) = 23 Hz, 1P, dppe), 68.9 (d, J(PP) = 23 Hz, 1P, dppe). ES-MS (m/z): 740, [M –  $H + Na]^+$ ; 565,  $[Ru(dppe)Cp]^+$ .

With  $[Ru(=C=CH_2)(dppe)Cp]PF_{c}/LiMe$ . A solution of  $[Ru(=C=CH_2)(dppe)Cp]PF_{c}/LiMe$ .  $C=CH_2$  (dppe) Cp PF<sub>6</sub> (150 mg, 0.204 mmol) in thf (15 mL) at -78 °C was treated with MeLi (0.27 mL, 1.5 M in hexane, 0.408 mmol). After 40 min tcne (29 mg, 0.224 mmol) was added to the mixture. After the mixture was warmed to room temperature, the color changed from yellow to purple. After the mixture was stirred for 1 h, solvent was removed and the residue was purified by preparative TLC  $(CH_2Cl_2)$ , giving Ru{C = CC(CN) = C(CN)\_2 (dppe)Cp (4) as a purple solid (97 mg, 69%). X-ray-quality crystals were grown from CDCl<sub>3</sub>-MeOH. Anal. Calcd (C<sub>38</sub>H<sub>29</sub>N<sub>3</sub>P<sub>2</sub>Ru): C, 66.08; H, 4.23; N, 6.08; M, 691. Found: C, 66.08; H, 4.35; N, 6.02. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>):  $\nu(C \equiv N)$  2212 w,  $\nu(C \equiv C)$  1990 vs,  $\nu(C = C)$  1462 m, 1410 w. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.46, 2.88 (2m, 2 × CH<sub>2</sub>, dppe), 5.02 (s, 5H, Cp), 7.19-7.76 (m, Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  28.34 (m, PCH<sub>2</sub>CH<sub>2</sub>P), 86.84 (s, Cp), 113.51, 115.40, 115.55 (3s, CN), 117.55 (s, C), 128.38–138.83 (m, Ph). <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ 84.6 (s, 2P, Ru(dppe)). ES-MS (m/z): 714,  $[M + Na]^+$ .

With  $Ru(C \equiv CH)(dppe)Cp^*$ . A stirred solution of  $Ru(C \equiv CH)$ -(dppe)Cp\* (500 mg, 0.758 mmol) in thf (20 mL) was treated with tcne (102 mg, 0.796 mmol). The solution instantaneously turned from yellow to purple and was stirred at room temperature for a further 30 min before the solvent was removed under reduced pressure. The residue was taken up in a minimal amount of  $CH_2Cl_2$  and purified by flash chromatography (silica,  $CH_2Cl_2$ -hexanes, 3:1). The first purple fraction afforded Ru{C=CC(CN)=C(CN)<sub>2</sub>}(dppe)Cp\* (5) as a purple solid (538 mg, 93%). X-ray-quality crystals were grown from CH<sub>2</sub>Cl<sub>2</sub>-hexane. Anal. Calcd (C<sub>43</sub>H<sub>39</sub>N<sub>3</sub>P<sub>2</sub>Ru): C, 67.88; H, 5.17; N, 5.52; *M*, 761. Found: C, 67.90; H, 5.25; N, 5.60. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>):  $\nu$ (C=N) 2199 w, 2209 m;  $\nu$ (C=C) 1979 vs;  $\nu$ (C=C) 1463 s, 1435 w. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.58 (s, 15H, Cp\*), 2.23, 2.82 (2m, 2 × CH<sub>2</sub>, dppe), 7.16–7.44 (m, Ph). <sup>13</sup>C NMR: in CDCl<sub>3</sub>,  $\delta$  10.29 (C<sub>3</sub>Me<sub>5</sub>), 29.03–29.65 (m, PCH<sub>2</sub>CH<sub>2</sub>P), 97.75 (s, C<sub>5</sub>Me<sub>5</sub>), 116.55, 138.22 (2s, C), 113.72, 116.12, 116.46 (3s, CN), 128.04–135.55 (m, Ph) 221.30 (t, *J*(CP) = 21 Hz, Ru–C); in C<sub>6</sub>D<sub>6</sub>,  $\delta$  9.91 (C<sub>5</sub>Me<sub>5</sub>), 28.70–34.29 (m, PCH<sub>2</sub>CH<sub>2</sub>P), 80.41, 118.48 (2s, C), 97.44 (s, C<sub>5</sub>Me<sub>5</sub>), 114.56, 116.09, 116.50 (3s, CN), 128.07–136.77 (m, Ph), 215.52 (m, C–Ru). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  80.0 (s, 2P, Ru(dppe)). ES-MS (m/z): 784, [M + Na]<sup>+</sup>.

With  $[Ru(=C+CH_2)(dppe)Cp^*]PF_6$  /LiMe. A solution of  $[Ru(=C+CH_2)(dppe)Cp^*]PF_6$  (90 mg, 0.113 mmol) in thf (15 mL) at -78 °C was treated with LiMe (0.09 mL, 2.5 M in hexane, 0.225 mmol). After 25 min tcne (14 mg, 0.113 mmol) was added to the mixture. The solution changed through orange-brown (5 min) to maroon (10 min). After it was stirred overnight, the solution was purple. The solvent was removed, and purification by preparative TLC (CH<sub>2</sub>Cl<sub>2</sub>) gave Ru{C=CC(CN)=C(CN)<sub>2</sub>}(dppe)Cp\* (5; 72 mg, 95%).

With  $Ru(C \equiv CC \equiv CH)(dppe)Cp^*$ . A stirred solution of  $Ru(C \equiv$ CC≡CH)(dppe)Cp\* (53 mg, 0.077 mmol) in thf (12 mL) was cooled to -78 °C, and tcne (11 mg, 0.086 mmol) was added. After 30 min the yellow solution had turned blue. The reaction mixture was left overnight with no further color change. Solvent was removed, and the residue was purified by preparative TLC (CH<sub>2</sub>Cl<sub>2</sub>). The major blue band afforded  $Ru\{C \equiv CC[=C(CN)_2]CH = C(CN)_2\}(dppe)$ -Cp\* (6) as a dark blue solid (30 mg, 48%). Anal. Calcd (C<sub>46</sub>H<sub>40</sub>N<sub>4</sub>P<sub>2</sub>Ru): C, 68.05; H, 4.97; N, 6.90; M, 812. Found: C, 68.09; H, 5.03; N, 6.79. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>):  $\nu$ (C $\equiv$ N) 2209 m,  $\nu$ (C $\equiv$ C) 1964 vs,  $\nu$ (C=C) 1450 br. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.42 (s, 15H, Cp\*), 1.93-2.17, 2.76-2.94 (2m, 2 × CH<sub>2</sub>, dppe), 6.37 (s, 1H, C=CH), 7.00-7.57 (m, Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  10.27 (C<sub>5</sub>Me<sub>5</sub>), 29.21-30.47 (m, PCH<sub>2</sub>CH<sub>2</sub>P), 75.70, 88.95, 138.85 (3s, C), 95.57 (s, C5Me5), 110.70, 112.81, 116.79, 116.81 (4s, CN), 128.29-138.45 (m, Ph), 155.90 (s, C=CH), 222.23 (m, Ru- $C_{\alpha}$ ). <sup>31</sup>P NMR ( $C_6D_6$ ):  $\delta$  81.4 (s, 2P, Ru(dppe)). ES-MS (MeCN, m/z): 813, [M + H]

Protonation of Ru{C=CC(CN)=C(CN)<sub>2</sub>}(dppe)Cp\* (5). A solution of  $Ru{C \equiv CC(CN) = C(CN)_2}(dppe)Cp^*$  (5; 116 mg, 0.152 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was protonated using either HBF<sub>4</sub>·OEt<sub>2</sub> (1.05 equiv) or HPF<sub>6</sub> (aqueous, 60%, 0.022 mL, 0.16 mmol). The stirred solution changed from dark purple to orange after 3 min. Solvent was removed, and the residue was taken up in CH<sub>2</sub>Cl<sub>2</sub> and added to hexane (60 mL) to give an orange-red precipitate of  $[Ru{=C=CHC(CN)=C(CN)_2}(dppe)Cp^*]X ([7]X; X = BF_4,$  $PF_6$ ) (89–92%). X-ray-quality crystals of the BF<sub>4</sub> salt were grown from CH<sub>2</sub>Cl<sub>2</sub>-hexane. Anal. Calcd (C<sub>43</sub>H<sub>40</sub>F<sub>6</sub>N<sub>3</sub>P<sub>3</sub>Ru): C, 56.96; H, 4.45; N, 4.63; M (cation), 762. Found: C, 56.87; H, 4.51; N, 4.60. IR (Nujol, cm^-1):  $\nu(C{\equiv}N)$  2216 m,  $\nu(C{=}C)$  1612 s.  $^1H$  NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 1.72 (s, 15H, Cp\*), 2.61, 2.97 (2m, 2 x CH<sub>2</sub>, dppe), 4.54 (s, 1H, C=CH), 7.12-7.70 (m, 20H, Ph). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ 10.89 (C<sub>5</sub>Me<sub>5</sub>), 27.84–28.76 (m, PCH<sub>2</sub>CH<sub>2</sub>P), 78.92 (s, C), 107.67 (s,  $C_{\rm s}$ Me<sub>5</sub>), 110.84, 112.04, 113.04 (3s, CN) 113.92 (s, C=CH, shown by DEPT NMR), 127.67–133.54 (m, Ph), 333.20 (t, J(CP) = 15 Hz, Ru=C). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  67.4 (s, 2P, Ru(dppe)). ES-MS (MeCN, m/z) 635, [Ru(dppe)Cp\*]<sup>+</sup>; 676, [Ru(NCMe)(dppe)- $Cp^*]^+$ ; 1545,  $[2(M - H) + Na]^+$ ; 784,  $[M - H + Na]^+$ ; 762,  $M^+$ ; 735,  $[M - HCN]^+$ .

**Reactions of Ru{C=CC(CN)=C(CN)\_2}(dppe)Cp\* (5) with MClL**<sub>n</sub>. General Conditions. A mixture of Ru{C=CC(CN)=  $C(CN)_2$ (dppe)Cp\* (5; 1 equiv), MClL<sub>n</sub> (1 equiv), and  $[NH_4]PF_6$ (4 equiv) was heated in refluxing MeOH. In all cases, the solution changed from deep purple to dark blue. The solution was cooled to room temperature, and the blue crystalline material was collected upon a sinter and washed with methanol (2 × 3 mL) and hexane (5 mL) to give the product.

0.079 mmol), RuCl(dppe)Cp\* (53 mg, 0.079 mmol), and [NH<sub>4</sub>]PF<sub>6</sub> (51 mg, 0.315 mmol) in MeOH (8 mL, 90 min),  $[{Cp*(dppe)Ru}{u-C \equiv CC(CN) = C(CN)CN}{Ru(dppe)Cp*}]$ PF<sub>6</sub> ([8]PF<sub>6</sub>; 82 mg, 68%) was obtained as dark blue crystals. X-rayquality crystals were grown from CDCl<sub>3</sub>-hexane. Anal. Calcd (C<sub>79</sub>H<sub>78</sub>F<sub>6</sub>N<sub>3</sub>P<sub>5</sub>Ru<sub>2</sub>): C, 61.59; H, 5.10; N, 2.73; M (cation), 1396. Found: C, 61.36; H, 5.17; N, 2.72. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): *ν*(C≡N) 2209 w,  $\nu$ (C $\equiv$ C) 1963 vs,  $\nu$ (Ph–CH) coupled with  $\nu$ (Cp\* C–H) 1604 w,  $\nu$ (C=C) 1448 s, 1436 s. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.55, 1.46 (2s, 15H, Cp\*), 2.24–2.52 (br m,  $3 \times CH_2$ , dppe), 2.71–2.79 (m,  $1 \times CH_2$ , dppe), 7.09–7.50 (m, Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  9.82 (C<sub>5</sub>Me<sub>5</sub> (Ru–  $N \equiv C$ )), 10.10 (C<sub>5</sub>Me<sub>5</sub> (Ru-C $\equiv C$ )) 28.21-29.97 (m, 2 × PCH<sub>2</sub>CH<sub>2</sub>P), 93.51 (s, C<sub>5</sub>Me<sub>5</sub> (Ru-N=C)), 98.71 (s, C<sub>5</sub>Me<sub>5</sub> (Ru-C=C)), 102.61, 124.23, 145.61 (3s, C), 113.92, 115.22 (2s, CN), 128.22–136.01 (m, Ph). <sup>31</sup>P NMR (CDCl<sub>2</sub>):  $\delta$  79.8 (s, 2P, Cp\*(dppe)Ru(C≡C)), 75.0 (s, 2P, Cp\*(dppe)Ru(N≡C)), -142.9 (sept,  $\tilde{J}(PF) = 711$  Hz, 1P, PF<sub>6</sub>). ES-MS (MeOH, m/z): 1396, M<sup>+</sup>; 635, [Ru(dppe)Cp\*]<sup>+</sup>.

 $[{Cp*(dppe)Ru}_{\mu-C} = CC(CN) = C(CN)CN} {Os(dppe)Cp*}]PF_{6}$ ([9] $PF_6$ ). From Ru{C = CC(CN) = C(CN)\_2}(dppe)Cp\* (52 mg, 0.072 mmol), OsCl(dppe)Cp\* (52 mg, 0.072 mmol), and [NH<sub>4</sub>]PF<sub>6</sub> (47 mg, 0.287 mmol) in MeOH (7 mL, 24 h),  $[{Cp*(dppe)Ru}{\mu-C \equiv CC(CN) = C(CN)CN} Os(dppe)Cp*]]$ PF<sub>6</sub> ([9]PF<sub>6</sub>; 58 mg, 50%) was obtained as dark blue microcrystals. Single crystals suitable for X-ray diffraction were grown from CH<sub>2</sub>Cl<sub>2</sub>hexane. Anal. Calcd (C<sub>79</sub>H<sub>78</sub>F<sub>6</sub>N<sub>3</sub>P<sub>5</sub>OsRu): C, 58.22; H, 4.82; N, 2.58; M (cation), 1486. Found: C, 58.24; H, 4.84; N, 2.61. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>):  $\nu$ (C $\equiv$ N) 2206 w, 2158 w,  $\nu$ (C $\equiv$ C) 1964 vs,  $\nu$ (C=C) 1445 w, 1436 m. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.55 (s, 30H, 2 × Cp\*), 2.30 (br m, 1 × CH<sub>2</sub>, dppe), 2.44–2.49 (br m, 2 × CH<sub>2</sub>, dppe), 2.74 (m, 1 × CH<sub>2</sub>, dppe), 7.12–7.48 (m, Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  9.54 (C<sub>5</sub>Me<sub>5</sub> (Os– N≡C)), 10.13 (C<sub>5</sub>Me<sub>5</sub> (Ru−C≡C)), 29.47−31.06 (m, 2 × PCH<sub>2</sub>CH<sub>2</sub>P), 90.84 (s, C<sub>5</sub>Me<sub>5</sub> (Os−N≡C)), 98.50 (s, C<sub>5</sub>Me<sub>5</sub> (Ru- $C \equiv \overline{C}$ )), 128.22–136.01 (m, Ph). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  79.7 (s, 2P, Cp\*(dppe)Ru−(C≡C)), 41.3 (s, 2P, Cp\*(dppe)Os−(N≡C)), -142.5 (sept, J(PF) = 710 Hz, 1P,  $PF_6$ ). ES-MS (MeOH, m/z):

1486, M<sup>+</sup>; 725,  $[Os(dppe)Cp^*]^+$ ; 635,  $[Ru(dppe)Cp^*]^+$ .  $[{Cp^*(dppe)Ru}_{\mu-C} \subset (CN) = C(CN)CN}_{Ru}(PPh_3)_2Cp}]PF_6$ ([10] $PF_6$ ). From Ru{C  $\equiv$  CC(CN)=C(CN)<sub>2</sub>}(dppe)Cp\* (55 mg, 0.072 mmol), RuCl(PPh<sub>3</sub>)<sub>2</sub>Cp (52 mg, 0.072 mmol), and [NH<sub>4</sub>]PF<sub>6</sub> (47 mg, 0.288 mmol) in MeOH (8 mL, 30 min), [{Cp\*(dppe)Ru}{µ- $C \equiv CC(CN) = C(CN)CN \{ Ru(PPh_3)_2 Cp \} ] PF_6 \quad ([10]PF_6; 59 mg,$ 51%) was obtained as dark blue crystals. X-ray-quality crystals were grown from CDCl<sub>3</sub>-hexane. Anal. Calcd (C<sub>84</sub>H<sub>74</sub>F<sub>6</sub>N<sub>3</sub>P<sub>5</sub>Ru<sub>2</sub>): C, 63.19; H, 4.76; N, 2.63; M (cation), 1451. Found: C, 62.82; H, 4.76; N, 2.66. IR  $(CH_2Cl_2, cm^{-1})$ :  $\nu(C\equiv N)$  2210 w, 2165 w,  $\nu(C\equiv C)$ 1961 vs,  $\nu$ (C=C) 1481 w, 1436 s. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.60 (s, 15H, Cp\*), 2.37, 2.88 (2m,  $2 \times CH_2$ , dppe), 4.48 (s, 5H, Cp), 7.04–7.50 (m, Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  10.23 (C<sub>5</sub>Me<sub>5</sub>), 29.43 (m, PCH<sub>2</sub>CH<sub>2</sub>P), 84.36 (s, C<sub>5</sub>H<sub>5</sub>), 99.19 (s, C<sub>5</sub>Me<sub>5</sub>), 97.83, 104.42, 149.68 (3s, C), 113.69, 114.66, 115.25 (3s, CN), 127.63-136.45 (m, Ph). <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ 79.5 (s, 2P, Ru(dppe)Cp\*), 41.3 (s, 2P,  $Ru(PPh_3)_2Cp)$ , -142.5 (sept, J(PF) = 709 Hz, 1P, PF<sub>6</sub>). ES-MS (MeOH, m/z): 1451, M<sup>+</sup>; 691,  $[Ru(PPh_3)_2Cp]^+$ .

 $[{Cp*(dppe)Ru}_{\mu-C} \subset C(CN) = C(CN)CN}{trans-RuCl(dppe)}]PF_6$ ([11] $PF_6$ ). The product from Ru{C  $\equiv$  CC(CN)=C(CN)<sub>2</sub>}(dppe)-Cp\* (80 mg, 0.105 mmol), cis-RuCl<sub>2</sub>(dppe)<sub>2</sub> (51 mg, 0.053 mmol), and [NH<sub>4</sub>]PF<sub>6</sub> (68 mg, 0.420 mmol) in MeOH (10 mL, 24 h) was purified by column chromatography (silica). Unreacted purple  $Ru{C \equiv CC(CN) = C(CN)_2}(dppe)Cp^*$  first eluted with  $CH_2Cl_2$ , while with acetone-hexane (1:1), a blue fraction containing  $[{Cp*(dppe)Ru}{\mu-C \equiv CC(CN) = C(CN)CN}{trans-RuCl}$  $(dppe)_2$ }PF<sub>6</sub> ([11]PF<sub>6</sub>; 42 mg, 43%) was obtained. Anal. Calcd (C<sub>95</sub>H<sub>89</sub>F<sub>6</sub>N<sub>3</sub>P<sub>7</sub>Ru<sub>2</sub>): C, 61.97; H, 4.87; N, 2.28; M (cation), 1696. Found: C, 61.84; H, 4.90; N, 2.35. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): *ν*(C≡N) 2207 w,  $\nu(C{\equiv}C)$  1964 vs,  $\nu(C{=}C)$  1605 w, 1484 w, 1436 m.  $^1H$  NMR  $(CDCl_3): \delta 1.57 \text{ (s, 15H, Cp*), 2.35 (br m, 1 × CH<sub>2</sub>, dppe) 2.62 (br$ m,  $2 \times CH_2$ , dppe), 2.81 (m,  $3 \times CH_2$ , dppe), 7.01–7.58 (m, Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz):  $\delta$  10.10 (C<sub>5</sub>Me<sub>5</sub>), 29.26–29.91 (m, 3 × PCH<sub>2</sub>CH<sub>2</sub>P), 98.73, 102.66, 124.62, 148.11 (4s, C), 99.16 (s, C<sub>5</sub>Me<sub>5</sub>),

#### Table 11. Crystal Data and Refinement Details for 2-Ru, 3-5, [7]BF<sub>4</sub>, [9]PF<sub>6</sub>, and [10]PF<sub>6</sub>

	2-Ru	3	4	5
formula	C48H35N3P2Ru	C <sub>39</sub> H <sub>30</sub> N <sub>4</sub> P <sub>2</sub> Ru·CH <sub>2</sub> Cl <sub>2</sub>	$C_{38}H_{29}N_3P_2Ru$	C43H39N3P2Ru
MW	816.80	802.61	690.65	760.78
cryst syst	monoclinic	triclinic	orthorhombic	monoclinic
space group	$P2_1/n$	$P\overline{1}$	$Pca2_1$	$P2_1/n$
a/Å	11.4978(7)	11.7459(5)	21.433(2)	13.362(3)
b/Å	17.5630(9)	11.9723(5)	16.439(1)	17.193(4)
c/Å	19.605(1)	13.2917(6)	17.989(2)	16.114(4)
$\alpha/\deg$		82.087(4)		
$\beta/\deg$	100.135(1)	89.623(4)		98.964(4)
γ/deg		75.665(4)		
$V/Å^3$	3897	1793	6338	3657
$\rho_{\rm c}/{\rm g~cm^{-3}}$	1.392	1.487	1.448	1.382
Z	4	2	8	4
$2\theta_{\rm max}/{\rm deg}$	75	60	67	50
$\mu$ (Mo K $\alpha$ )/mm <sup>-1</sup>	0.52	0.71	0.63	0.55
$T_{\min/\max}$	0.82	0.94	0.86	0.62
cryst dimens/mm <sup>3</sup>	$0.45 \times 0.38 \times 0.35$	$0.20 \times 0.18 \times 0.13$	$0.48 \times 0.16 \times 0.10$	$0.52 \times 0.18 \times 0.03$
N <sub>tot</sub>	81 052	19 495	89 975	35 617
$N(R_{\rm int})$	20 404 (0.022)	9313 (0.038)	23 867 (0.054)	6472 (0.109)
No	17 661	5735	17 574	4584
R1	0.027	0.040	$0.048^{a}$	0.057
wR2 (a (,b))	0.075 (0.036, 1.4)	0.088 (0.038)	0.117 (0.052, 5.4)	0.148 (0.079, 2.5)
T/K	150	100	150	100
	$[7]BF_4$		[9]PF <sub>6</sub>	[ <b>10</b> ]PF <sub>6</sub>
formula	$C_{43}H_{40}N_3P_2Ru\cdot BF_4$		$C_{79}H_{78}N_3OsP_4Ru\cdot F_6P$	C <sub>84</sub> H <sub>74</sub> N <sub>3</sub> P <sub>4</sub> Ru <sub>2</sub> ·F <sub>6</sub> P
MW	848.60		1629.56	1596.45
cryst syst	monoclinic		monoclinic	orthorhombic
space group	$P2_1/n$		C2/c	Fdd2
a/Å	11.1286(2)		20.9050(10)	36.72(2)
b/Å	17.4916(3)		14.7607(8)	68.84(3)
c/Å	20.1481(4)		23.7010(10)	11.415(5)
$\beta/\deg$	103.473(2)		100.138(5)	
$V/Å^3$	3814		7199	28 857
$\rho_{\rm c}/{\rm g~cm^{-3}}$	1.47 <sub>8</sub>		1.502	1.470
Z	4		4	16
$2\theta_{\rm max}/{\rm deg}$	68		62	55
$\mu$ (Mo K $\alpha$ )/mm <sup>-1</sup>	0.55		2.15	0.59
$T_{\min/\max}$	0.80		0.81	0.85
cryst dimens/mm <sup>3</sup>	$0.34 \times 0.24 \times 0.03$		$0.23 \times 0.20 \times 0.10$	$0.60 \times 0.12 \times 0.10$
N <sub>tot</sub>	75 979		51 366	47 047
$N(R_{\rm int})$	15 394 (0.072)		10 772 (0.077)	15 861 (0.072)
No	8061		5503	10 929
R1	0.042		0.075	0.062 <sup>b</sup>
wR2 (a (,b))	0.097 (0.043)		0.204 (0.075, 43)	0.16 (0.056, 243)
T/K	100		100	150
${}^{a}x_{abs} = -0.02(10). {}^{b}x_{abs} = 0.0$	2(4).			

112.01, 113.73, 115.62 (3s, CN), 127.22–136.00 (m, Ph). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  80.1 (s, 2P, Cp\*(dppe)Ru), 43.2 (s, 4P, RuCl(dppe)<sub>2</sub>), -142.5 (sept, *J*(PF) = 710 Hz, 1P, PF<sub>6</sub>). ES-MS (MeOH, *m*/*z*): 1696, M<sup>+</sup>; 933, [RuCl(dppe)<sub>2</sub>]<sup>+</sup>; 635, [Ru(dppe)Cp\*]<sup>+</sup>.

**Structure Determinations.** Full spheres of diffraction data were measured using CCD area-detector instrumentation.  $N_{\text{tot}}$  reflections were merged to N unique ( $R_{\text{int}}$  cited) after "empirical"/multiscan absorption correction (proprietary software),  $N_{\text{o}}$  with  $F > 4\sigma(F)$  being considered "observed"; all data were used in the full matrix least-squares refinements on  $F^2$ . All data were measured using monochromatic Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Anisotropic displacement parameter forms were refined for the non-hydrogen atoms, (x, y, z,  $U_{\text{iso}}$ )<sub>H</sub> being included following a "riding" model

(reflection weights  $(\sigma^2(F^2) + (aP)^2 (+ bP))^{-1} (P = (F_o^2 + 2F_c^2)/3))$ . Neutral atom complex scattering factors were used; computation used the SHELXL 97 program.<sup>69</sup> Pertinent results are given in the figures (which show non-hydrogen atoms with 50% probability amplitude displacement ellipsoids) and in Tables 1 and 11.

*Variata.* [8]*PF*<sub>6</sub>. As refined in space group C2/c, with a centrosymmetric cation, three of the four phenyl rings were modeled as disordered over pairs of sites, with occupancies 0.5, as were also the fluorine atoms. In the isomorphous [9]*PF*<sub>6</sub>, all phenyl rings were modeled as disordered, with isotropic adp forms; the metal atom was modeled as a Ru/Os composite. The pendant ligand atom at the metal was modeled as a C/N composite.

#### ASSOCIATED CONTENT

#### Supporting Information

Text giving details of the computational work, tables giving the energy and Cartesian coordinates of the optimized geometries of **5**', 7', and **8**', and CIF files giving all crystallographic data for **2-Ru**, **3–5**, [7]BF<sub>4</sub>, [9]PF<sub>6</sub>, and [10]PF<sub>6</sub>. 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 705431–705435, 707491, and 707492. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (Fax: + 44 1223 336 033; e-mail: deposit@ ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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#### DEDICATION

Dedicated to the memory of Professor F. G. A. Stone, organometallic chemist extraordinaire, respected mentor, and valued friend of M.I.B.

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