ORGANOMETALLICS

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pubs.acs.org/Organometallics

Polarized Complexes Obtained by Regiospecific Substitution of a CN Group in Ru{C≡CC(CN)=C(CN)$_2$}(dppe)Cp* (Cp* = η-C$_5$Me$_5$)

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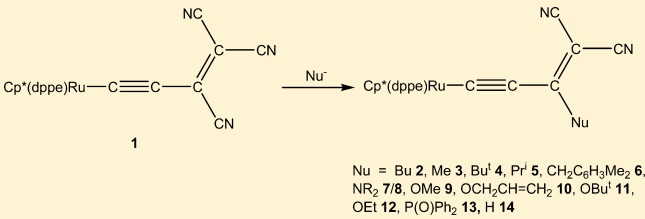
Supporting Information

ABSTRACT: The complex Ru{C≡CC(CN)=C(CN)$_2$}(dppe)Cp* (**1**), containing the new tricyanovinylethynyl (3,4,4-tricyanobut-3-en-1-ynyl) ligand, undergoes ready substitution of the 3-cyano group by nucleophiles (Nu) such as H, Me, Pr^i, Bu, Bu^t, mesityl, OMe, OBu^t, OCH$_2$CH=CH$_2$, NHEt, NEt$_2$, and PPh$_2$ to give Ru{C≡CC(Nu)=C(CN)$_2$}(dppe)Cp*. The X-ray diffraction structures of several of the resulting complexes are reported and, for the mesityl and PPh$_2$ products, show that isomerization to the 3,5-dimethylbenzyl and oxidation to the phosphine oxide have respectively occurred.



INTRODUCTION

Although reactions of tetracyanoethene ((NC)$_2$C=C(CN)$_2$, TCNE) with alkynyl–transition-metal complexes generally proceed by [2 + 2] cycloaddition reactions to give tetracyanocyclobutenyls with subsequent ring opening to afford tetracyanobutadienyls,[1] we recently found that facile substitution of a CN group in TCNE by the ethynyl groups of complexes M(C≡CH)(PP)Cp′ (M = Ru, (PP)Cp′ = (PPh$_3$)$_2$Cp, (dppe)Cp*; M = Os, (PP)Cp′ = (dppe)Cp*), with concomitant elimination of HCN, afforded the unusual tricyanovinylethynyl (tricyanobutenynyl) complexes M{C≡CC(CN)=C(CN)$_2$}(PP)Cp′.[2] The C≡C triple bonds in these complexes are strongly polarized by virtue of their linking an electron-rich M(PP)Cp′ fragment to the powerfully accepting =C(CN)$_2$ group. Such materials, which can be considered to contain an electron-rich metal donor (D) linked by a π-conjugated bridge (π) to a strongly electron-accepting group (A) (D–π–A systems), are of contemporary interest because their strong polarization leads to efficient nonlinear optical properties, which may have a role in the construction of various molecular-scale electronic devices.[3] Their structural features are consistent with a significant contribution from the zwitterionic mesomer, and we decided to examine the chemistry of these systems in more detail.

Part of the extensive chemistry of tetracyanoethene is characterized by substitution of one or two CN groups by other nucleophiles.[4,5] For example, alcohols such as MeOH and HOCH$_2$CH$_2$OH react under basic conditions to give respectively methyl tricyanovinyl ether, MeOC(CN)=C(CN)$_2$, and dicyanoketene acetal, (NC)$_2$C=C(OCH$_2$CH$_2$O). Similarly, arylamines and phosphorus ylides afford tricyanovinyl–anilines and –phosphorylides, respectively.[4−7] The ruthenium complex Ru{C≡CC(CN)=C(CN)$_2$}(dppe)Cp* (**1**) was obtained in essentially quantitative yield, and we have commenced a study of its reactions. In an earlier account, we described complexes formed by addition of a proton or other metal–ligand fragments.[2b] In this paper, we direct our attention to the facile substitution of the CN group *gem* to the metal center by other nucleophiles, which provides a route for tuning the electronic properties of these molecules. While the negative charge can be accommodated by the dicyanomethylene group, the CN group *gem* to the metal substituent is labilized thereby, as shown by the longer C–CN distance (1.477(8) Å) in comparison with those of the =C(CN)$_2$ group (1.441, 1.449(2) Å). A brief account of some of these reactions has appeared.[2a]

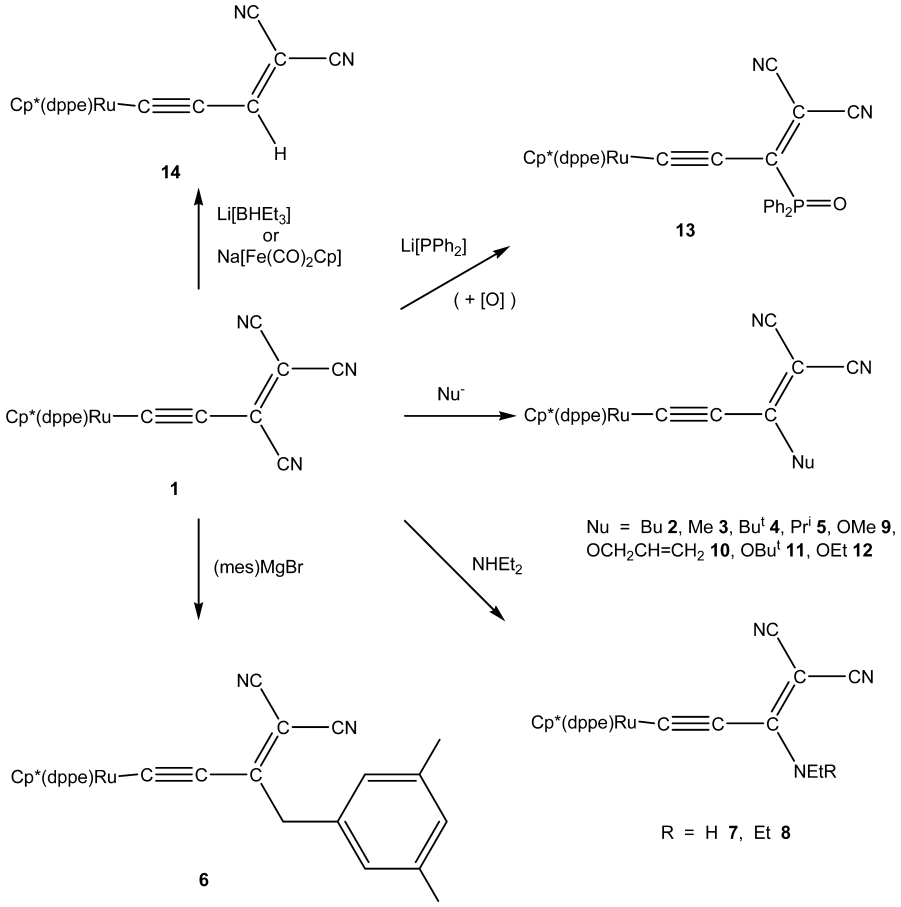
RESULTS

Substitution Reactions of Ru{C≡CC(CN)=C(CN)$_2$}(dppe)Cp* (1). The propensity for substitution of the CN group *gem* to the metal center was discovered accidentally from a reaction between **1** and the putative LiC≡C{Ru(dppe)Cp*} derivative[8] (obtained from LiBu and Ru(C≡CH)(dppe)Cp*), designed to give the binuclear complex {Cp*(dppe)Ru}$_2$C=C(CN)$_2$. In fact, only the dicyanobutenynyl Ru{C≡CCBu=C(CN)$_2$}(dppe)Cp* (**2**), as shown by a single-crystal X-ray diffraction study (see below), was obtained. Earlier work by others had described a reaction between the analogous indenyl complex Ru(C≡CH)(PP)(η^5-C$_9$H$_7$) (PP = (PPh$_3$)$_2$, dppe) and LiBu to give a lithiated alkynyl intermediate which could be converted to Ru(C≡CR)(PP)(η^5-C$_9$H$_7$) when treated with

Received: January 24, 2012
Published: May 22, 2012

   dx.doi.org/10.1021/om300059q | *Organometallics* 2012, 31, 4174–4181

Scheme 1. Reactions of Ru{CCC(CN)=C(CN)$_2$}(dppe)Cp* (1) with Nucleophiles



RX (RX = SnClPh$_3$, [I(py)$_2$]BF$_4$).[8] We then realized that the formation of **2** might proceed via substitution of the CN group *gem* to the metal center in **1** by unreacted LiBu with elimination of LiCN. This hypothesis was supported by the direct reaction between **1** and LiBu, which gave **2** in 32% yield.

We have now found that **1** readily reacts with a range of nucleophiles to give similar products **2**–**14** (Scheme 1), many of which have been characterized by single-crystal X-ray diffraction studies. All compounds described herein gave satisfactory elemental analyses. Spectroscopic properties, detailed in the Experimental Section, are also in accord with the assigned structures, IR spectra containing characteristic absorptions assigned to ν(CN) between 2170 and 2214 (two bands) and a ν(C≡C) band between 1979 and 1995 cm^{-1} (except for **7** and **8**, where the absorption is at 2019 and 2014 cm^{-1}, respectively, and **13**, where it is found at 1958 cm^{-1}). Unusually strong ν(C≡C) bands were found, resulting from the polarization of the C≡C triple bond by the electron-donating and -accepting substituents. At lower frequencies, ν(C=C) bands occur at ca. 1485 cm^{-1}. In the NMR spectra, the metal–ligand fragment showed the usual Cp* (δ_H 1.55, δ_C 10.25, 95.5) and dppe (δ_H ca. 2.25, 2.90, δ_C ca. 29.5–30.5, δ_P 81.0–84.6) resonances. The cyanocarbon fragment gives rise to two closely spaced ^{13}C resonances at δ ca. 116–120. Carbon atoms in the C$_4$ chain were found at δ ca. 75, 120, 150, and 200, the last signal being a triplet (J(CP) ca. 23 Hz) and arising from C(1). It is likely that the signal at δ ca. 150 arises from the C(CN)$_2$ carbon, so that the other resonances can be assigned to C(2) and C(3). The various substituents at C(3) gave rise to the expected signals. ES-MS generally contain M$^+$ or [M + H]$^+$, [M + Na]$^+$, and [Ru(dppe)(C$_5$Me$_5$)]$^+$ ions, together with aggregate ions formed by clustering of two molecules around a Na$^+$ cation: e.g., [2 M + Na]$^+$.

Reactions between **1** and the organolithium reagents LiMe.LiBr and LiBu^t, or the Grignard reagent Pr^{i}MgBr, afforded the analogous complexes Ru{C≡CCR=C(CN)$_2$}(dppe)Cp* (R = Me (**3**; 76%), Bu^t (**4**; 27%), Pr^i (**5**; 48%), respectively). In contrast, reactions with LiPh or PhMgCl each gave several products, none of which could be obtained pure. However, with (mes)MgBr, the complex with R = CH$_2$C$_6$H$_3$Me$_2$-3,5 (**6**; 11%) could be isolated. This rearrangement of the mesityl (2,4,6-trimethylphenyl) group to the 3,5-dimethylbenzyl substituent was revealed by a single-crystal X-ray diffraction structure determination (see below). The 3,5-dimethylbenzyl group gives characteristic resonances for the two Me groups at δ 1.26, the CH$_2$ at δ 3.21, and the C$_6$H$_3$ protons at δ 6.39 and 6.76 (intensity 2/1). This unusual, although not unprecedented, isomerization is probably driven by steric pressures around C(3). Previous organometallic examples include conversion of Ir(mes)(CO)(dppe) to Ir(CH$_2$C$_6$H$_3$Me$_2$-3,5)(η-C$_2$H$_4$)(CO)(dppe) on heating in the presence of C$_2$H$_4$ and the formation of an equilibrium mixture of Ir{C(O)mes}(CO)$_2$(dppe) and *cis*- and *trans*-IrH{CH$_2$C$_6$H$_2$Me$_2$-3,5-C(O)-2}(CO)(dppe) by heating the C(O)mesityl complex in CO.[9]

Attempts to use alkynyl anions to displace the CN(3) group were unsuccessful, several complexes containing heterocyclic ligands having been isolated instead. These are probably

dx.doi.org/10.1021/om300059q | *Organometallics* 2012, 31, 4174–4181

formed by attack at a CN group and will be described elsewhere.

Nitrogen nucleophiles also displace the CN group, a reaction between **1** and $NHEt_2$ affording the two products Ru{C≡CC(NREt)=C(CN)$_2$}(dppe)Cp* (R = H (**7**; 23%), Et (**8**; 34%)). These complexes were readily separated by preparative TLC and were characterized on the basis of their ^{1}H NMR and ES-MS spectra. Of note are the IR ν(C≡C) bands at relatively high frequencies (2019 and 2014 cm^{-1}, respectively; cf. 1979 cm^{-1} in **1**), a result of the strong electron-donor property of the amino groups. Compound **7** has the NH resonance at δ_H 5.36. In particular, the ES-MS of these complexes (obtained from solutions containing NaOMe) contained $[M + Na]^+$ ions at *m*/*z* 802 and 830, respectively, while confirmation of the structure of **7** by an X-ray diffraction structure determination is reported below. Loss of an ethyl group from $NHEt_2$ during this reaction may result from activation of the NEt_2 group in **8** by the cyano carbon, perhaps resulting in a reaction similar to a β-elimination.

Addition of sodium to a solution of **1** in a mixture of THF and MeOH smoothly afforded Ru{C≡CC(OMe)=C(CN)$_2$}(dppe)Cp* (**9**; 36%), while a similar procedure using allyl alcohol afforded Ru{C≡CC(OCH$_2$CH=CH$_2$)=C(CN)$_2$}(dppe)Cp* (**10**; 22%). The OBu^t analogue **11** was obtained in 21% yield from **1** and KOBu^t. Addition of LiBr or LiCl to the reaction mixture, or using LiMe·LiBr, increased the yields of **10** and **11** to 42 and 54%, respectively, possibly by increasing the rate of substitution by stabilizing the negative charge in the transition state.[10−12] A further example of an alkoxy derivative was obtained from the reaction between **1** and HC≡CCO$_2$Et/Na[N(SiMe$_3$)$_2$], which afforded Ru{C≡CC(OEt)=C(CN)$_2$}(dppe)Cp* (**12**), possibly because the alkynyl ester is converted to the stronger nucleophile NaOEt more rapidly than reaction with **1** can occur. As mentioned above, complex products were obtained from reactions involving other (simpler) alkynyl anions. The NMR spectra of these complexes showed the expected signals for the OR groups.

Extension of these substitutions to a phosphorus nucleophile was achieved in the reaction between **1** and $LiPPh_2$. Conventional workup afforded a deep pink compound in 40% yield, which was identified as the phosphoryl derivative Ru{C≡CC[P(O)Ph$_2$]=C(CN)$_2$}(dppe)Cp* (**13**) by an X-ray structure determination. IR bands at 1958 cm^{-1} (ν(C≡C)) and a weak ν(PO) absorption at 1195 cm^{-1} in the IR spectrum also supported this formulation. It is likely that air oxidation of an initial PPh_2 product, whose presence was suggested by ^{31}P resonances at δ 30.5 and 81.0 (1/2) in the reaction mixture, which also contained signals at δ 23.6 and 83.3 (1/2) from the phosphoryl derivative **13**, occurs during reaction or workup.

Substitution of the CN(3) group by hydride was initially achieved in a reaction between **1** and Na[Fe(CO)$_2$Cp], and orange-red Ru{C≡CCH=C(CN)$_2$}(dppe)Cp* (**14**) was obtained in 89% yield. The direct reaction between **1** and Li[BHEt$_3$] in THF at −78 °C afforded **14** in 45% yield. The −CH− group gives resonances at δ_H 6.75 and δ_C 142.22. The unusual replacement of CN by H during the reaction between **1** and Na[Fe(CO)$_2$Cp] cannot be easily explained. There are analogous reactions in the formation of Fe{CH(CN)$_2$}(CO)$_2$Cp in the reaction of the same carbonylmetal anion with $CBr_2(CN)_2$[13] and of Fe(C$_6$F$_4$H-4)(CO)$_2$Cp from similar reactions of C_6F_5X (X = F, Cl, Br, I).[14] In all cases, the byproduct is {Fe(CO)$_2$Cp}$_2$, suggesting that radical reactions may be involved.

Electrochemistry and UV−Vis Spectroscopy. The redox properties of some of these compounds, which are summarized in Table 1, are also of interest. For **1** and **13**, reduction events

Table 1. Electrochemical and UV−Vis Data

	electrochemistry (V)			
R	E_{red}	E_{ox}^1	E_{ox}^2	λ_{max}/nm (ε/M^{-1} cm^{-1})
NEt_2 (**8**)		+0.53	+1.35^i	315 (14 600), 386 (17 600)
Bu^t (**4**)		+0.58	+1.23^i	456 (23 000)
H (**14**)		+0.64	+1.08^i	460 (26 900)
OMe (**9**)		+0.70	+1.17^i	416 (n.a.)
OBu^t (**11**)		+0.72	+1.38^i	426 (22 000)
$P(O)Ph_2$ (**13**)	−1.40	+0.69	+1.17^i	527 (18 900)
CN (**1**)	−1.06	+0.91^P		557 (26 200)

^{i}Irreversible. ^{P}Partially reversible (i_a/i_c = 0.8). n.a. = not available. All values in V vs SCE, referenced to $FeCp^*_2/[FeCp^*_2]^+$ = −0.02 V. Electrochemical samples (1 mM) were dissolved in CH_2Cl_2 containing 0.1 M $[NBu_4]PF_6$ as supporting electrolyte.

are found at −1.06 and −1.40 V vs SCE, respectively, which may reflect the presence of electron-withdrawing groups on C(3). The redox potentials (+0.53 V (NEt_2) to +0.91 V (CN)) correlate well with the UV−vis λ_{max} values (Table 1). At higher potentials, a second, irreversible, process is found at potentials which appear to be inversely related to the electron-donor power of the *gem* substituent: e.g., +1.08 (H) to +1.35 V (NEt_2). This process is not found for **1** within the solvent range employed.

These complexes are notable for the strong variation in their colors, through yellow (OR, NR_2), orange (alkyl), red-orange (H), and pink ($P(O)Ph_2$) to violet (CN), with differing substituents (Figure 1). A feature of the UV−vis spectra (Table

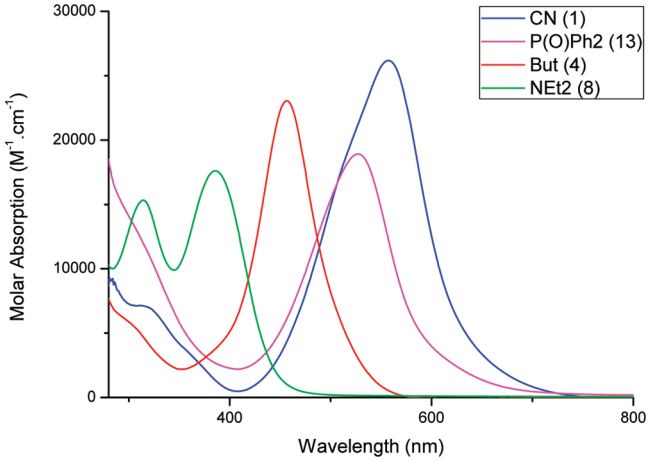


Figure 1. UV−vis spectra of Ru{C≡CC(R)=C(CN)$_2$}(dppe)Cp* in CH_2Cl_2; R = CN (**1**; blue trace), Bu^t (**4**; red trace), NEt_2 (**8**; green trace), $P(O)Ph_2$ (**13**; magenta trace).

1) is an intense absorption (ε ca. 20 000 M^{-1}.cm^{-1}), with λ_{max} ranging between 386 to 557 nm. This results from the polarization conferred by the presence of an electron-rich metal center and the strongly electrophilic cyanocarbon fragment linked by the C≡C core (D−π−A sytems). Changes in λ_{max} with different substituents at C(3) relate to the stronger electron-withdrawing substituent having the higher λ_{max} value, from 557 nm (for **1**) to 386 nm (in **8**). The latter has a second

dx.doi.org/10.1021/om300059q | Organometallics 2012, 31, 4174−4181

absorption band at 315 nm, perhaps because of the presence of a second strong electron donor (NEt_2).

As found for **1**,[2] complex **4** displays marked solvatochromism, the main absorption shifting from 456 nm (CH_2Cl_2) to 438 nm (hexane/CH_2Cl_2, 24/1). This feature supports the assignment of the strong absorption band to an M→L CT, as substantiated for **1** by the DFT calculations described elsewhere.[2b] Partial spatial overlap of the HOMO and LUMO allows a facile transition to occur. Similar effects found for other "push−pull" molecules, including some related substituted alkynyl−ruthenium complexes,[15] have been attributed to the stability of the excited state in more polar solvents.[16] In such molecules, optical properties are related to the polarizability of the π-bonding electrons in the bridging core.[17,18] However, unlike some related compounds, including cyano(ethynyl)ethenes, our complexes do not fluoresce, possibly because the metal center quenches any emissions.

Molecular Structures. The molecular structures of several of the complexes described above have been determined by single-crystal X-ray diffraction methods, our preliminary communication containing details for compounds **1** and **9**.[2a] Figure 2 depicts a single molecule of **3** (as representative of molecules of **2**, **4**, **6**, **7**, **13**, and **14**, similar plots of which are to be found in the Supporting Information as Figures S1−S6; selected structural data for all complexes studied are collected in Table 2 and Table S1 (Supporting Information)).

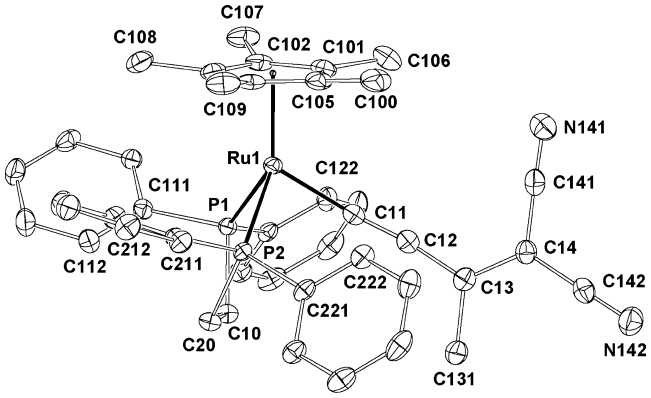


Figure 2. Projection of molecule 1 of Ru{C≡CCMe=C(CN)$_2$}(dppe)Cp* (**3**) as representative of complexes **2**, **4**, **6**, **7**, **13**, and **14** (projections of these molecules are given as Figures S1−S6 in the Supporting Information).

Common features for all molecules include the Ru(dppe)Cp* group, which has been described on many earlier occasions.[19] The present determinations confirm the presence of this pseudo-octahedral fragment, with Ru−C(cp*) = 2.234(2)−2.304(2) Å and Ru−P = 2.2665(4)−2.3093(6) Å and angles at Ru between 82.60(2) and 84.66(2)° (P(1)−Ru−P(2)) and between 81.17(7) and 92.97(6)° (P(1,2)−Ru−C(1)) (extreme values found in molecule 1 of **13**).

The alkynyl group is attached to Ru by a single bond (1.925(2)−1.977(6) Å, average 1.955(13) Å), the M−C≡C−C fragment being approximately linear (angles at C(1) 170.5(3)−178.8(6)° (average 175.7(24)°), angles at C(2) 167.9(2)−177.8(4)° (average 173.0(32)°), the short C(1)−C(2) separation (1.215(5)−1.234(8) Å, average 1.232(8) Å) confirming the retention of the C≡C triple bond. The similarity of the C(2)−C(3) (1.371(3)−1.428(4) Å, average 1.396(16) Å) and C(3)=C(4) bond lengths (1.368(8)−1.412(4) Å, average 1.386(18) Å) suggests considerable electron delocalization within this fragment (see below). The substituted vinyl group bears two CN groups on C(4) (C(4)−C(41,42) = 1.409(4)−1.437(8) Å, average 1.428(11) Å), while the second substituent on C(3), which reflects the substitution chemistry of **1**, is *gem* to the M−C≡C fragment. The substituents on C(3) are attached by C(3)−X bonds, where X = C (1.494(9)−1.541(5) Å, average 1.516(18) Å), N(3) (1.344(4), 1.345(4) Å), O(3) (1.349(3) Å, cf. 1.347(3) Å for **9**[2a]), P(3) (1.837(2), 1.845(2) Å). There are generally no significant differences in the Ru−C(1)−C(2)−C(3)−C(4) bond lengths (Table 2) as the substituent X attached to C(3) is changed, with the exception of **1** and **13**, in which X is strongly electron accepting. The geometrical parameters of these substituents are normal and do not merit further discussion.

DISCUSSION

The chemistry of TCNE is dominated by nucleophilic displacement of one or two CN groups,[4,5] a feature which we were able to use in the synthesis of compounds such as Ru{C≡CC(CN)=C(CN)$_2$}(dppe)Cp* (**1**) when sterically demanding alkynyl−group 8 metal complexes are used.[2] This reaction is an alternative to the [2 + 2] cycloaddition reactions which are usually found.[1] The likely mechanism involves stabilization of an intermediate charged species by the =C(CN)$_2$ group, followed by elimination of the CN(3) group as cyanide.

The present work has been concerned with the synthesis of a range of 3-substituted dicyanobutenynyl complexes from reactions between **1** and various nucleophiles. Thus, we have been able to replace the *gem* CN group by H, alkyl, amino, alkoxy, and phosphorus groups under mild conditions. In the last reaction, we suggest that the expected phosphine complex, containing an uncoordinated P(III) atom, is readily oxidized during the workup. The resulting complexes have been

Table 2. Bond Distances (Å) for Ru−C(1)≡C(2)−C(3)X=C(4)(CN)$_2$ Chains

X	Ru−C(1)	C(1)−C(2)	C(2)−C(3)X	C(3)=C(4)	ref
CN (**1**)	1.926(6)	1.243(7)	1.388(8)	1.368(8)	2
Bu (**2**)	1.959, 1.977(6)	1.234, 1.218(8)	1.395, 1.390(8)	1.393, 1.392(8)	this work
Me (**3**)	1.951, 1.957(2)	1.234, 1.232(2)	1.388, 1.391(2)	1.387, 1.379(2)	this work
Bu^t (**4**)	1.966(4)	1.215(5)	1.395(5)	1.393(5)	this work
$CH_2C_6H_3Me$ (**6**)	1.958(2)	1.229(3)	1.393(3)	1.376(3)	this work
NHEt (**7**)	1.966, 1.965(3)	1.232, 1.234(4)	1.418, 1.428(4)	1.404, 1.412(4)	this work
$P(O)Ph_2$ (**13**)	1.925, 1.936(2)	1.244, 1.241(3)	1.371, 1.376(3)	1.402, 1.397(3)	this work
H (**14**)	1.952(2)	1.231(3)	1.387(3)	1.383(3)	this work
OMe (**9**)	1.950(2)	1.237(3)	1.391(3)	1.388(3)	2a

dx.doi.org/10.1021/om300059q | *Organometallics* 2012, 31, 4174−4181

characterized spectroscopically and, in many cases, by single-crystal X-ray diffraction structure determinations. Their spectroscopic properties, in particular the NMR and UV−vis spectra, reflect the presence of the various substituents and their varying electron donor powers.

This chemistry is paralleled by the substitution chemistry of TCNE itself, e.g., in the reaction with 1,2-dihydroxyethane (ethylene glycol) to give $(NC)_2C{=}C(OCH_2CH_2O)$,[4,5] and is a result of the presence of good leaving groups on the alkene. Notable features of this chemistry include the enhanced yields obtained when alkylation reactions, for example, are carried out in the presence of metal halides[10−12] and the unusual, although not unprecedented,[9] isomerization of the expected mesityl complex to the 3,5-dimethylbenzyl derivative, perhaps driven by the steric requirements around C(3). In addition, the C(3)−CN bond in **1** (1.477(8) Å) is significantly longer than the other two C−CN bonds, a property consistent with the ready cleavage of the C(3)−CN bond during the reactions described above. The formation of both **7** and **8** from the reaction between **1** and $NHEt_2$ may result from competitive elimination of $(HCN + C_2H_4)$ and EtCN during the course of the reaction; we could not detect any NH_2Et in our sample of $NHEt_2$. The unusual replacement of CN by H during the reaction between **1** and $Na[Fe(CO)_2Cp]$ cannot be easily explained, although conversion of the anion to $\{Fe(CO)_2Cp\}_2$ suggests that radical reactions may be involved.

These complexes are further examples of "push−pull" compounds, in which an electron-rich center is linked via a conjugated carbon chain to a strongly electrophilic group (D−π−A systems).[16−18,20] As mentioned above, considerable work is currently directed toward the synthesis of purely organic molecules that fall into this category, which have potential as components in molecular electronics (optoelectronics, nonlinear optics).[198,21,22] Their absorptions across the visible region provide a measure of the HOMO−LUMO energy gap as a function of the electron-donor power of the 3-substituent, and the variations observed here indicate that subtle tuning of this gap is possible. The redox potentials, which decrease as the donor power of the 3-substituent increases, also provide a measure of these changes.

EXPERIMENTAL SECTION

General Considerations. 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 (20×20 cm^2) coated with silica gel (Merck, 0.5 mm thick) or by flash chromatography (Davisil 40−63 μm).

Instruments. IR spectra were obtained using a Bruker IFS28 FT-IR spectrometer. Unless otherwise stated, 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. NMR spectra were recorded on a Varian 2000 (^{1}H at 300.13 MHz, ^{13}C at 75.47 MHz, ^{31}P at 121.503 MHz) or Unity Inova 600 instrument, the latter being equipped with a cryoprobe (^{1}H at 599.653 MHz, ^{13}C at 150.796 MHz). Samples were dissolved in $CDCl_3$ contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane for ^{1}H and ^{13}C NMR spectra and external H_3PO_4 for ^{31}P NMR spectra. UV−vis−near-IR spectra were obtained with a Varian-Cary 5000 UV−vis−near-IR spectrophotometer. Samples were contained in fused quartz cells, path length 1 cm. Electrospray mass spectra (ES-MS) were obtained from samples dissolved in MeOH; in some cases, NaOMe was used as an aid to ionization.[23] Solutions were injected into a Fisons VG Platform II 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. CVs were recorded using a PAR Model 263A potentiostat, with a saturated calomel electrode. The cell contained a Pt-disk working electrode and Pt-wire counter and pseudoreference electrodes. Electrochemical samples (1 mM) were dissolved in CH_2Cl_2 containing 0.1 M $[NBu_4]PF_6$ as supporting electrolyte. Potentials are given in V vs SCE, referenced to $FeCp^*_2/[FeCp^*_2]^+$ (−0.02 V) as internal calibrant. Elemental analyses were by CMAS, Belmont, Victoria, Australia, and by Campbell Microanalytical Centre, University of Otago, Dunedin, New Zealand.

Reagents. The complex $Ru\{C{\equiv}CC(CN){=}C(CN)_2\}(dppe)Cp^*$ (**1**) was obtained as described previously.[2] All other reagents were obtained from Sigma-Aldrich or Fluka and used as received without further purification.

Preparation of $Ru\{C{\equiv}CCR{=}C(CN)_2\}(dppe)Cp^*$. *(a). R = Bu (2).* (i) A stirred solution of $Ru\{C{\equiv}CC(CN){=}C(CN)_2\}(dppe)Cp^*$ (**1**; 50 mg, 0.066 mmol) in thf (15 mL) was cooled to −78 °C and treated with LiBu (2.5 M in hexane, 29 μL, 0.073 mmol). The purple solution turned dark orange and was warmed to room temperature. Solvent was removed, and the residue was purified by preparative TLC (acetone/hexane, 3/7) to give some recovered starting material (R_f = 0.39; 5 mg, 10%). An orange band (R_f = 0.48) contained bright orange $Ru\{C{\equiv}CCBu{=}C(CN)_2\}(dppe)Cp^*$ (**2**; 15 mg, 30%, conversion 33%). X-ray-quality crystals were grown from hexane. Anal. Calcd ($C_{46}H_{48}N_2P_2Ru$): C, 69.77; H, 6.11; N, 3.54; M_r, 792. Found: C, 69.95; H, 6.32; N, 3.55. IR/cm^{-1}: ν(C≡N) 2210 w, ν(C≡C) 1989 vs, ν(C=C) 1483 m. ^{1}H NMR: δ 0.75 (t, J = 7 Hz, 3H, Me), 1.10 (m, 4H, 2 × CH_2), 1.56 (s, 15H, Cp*), 2.09 (t, J = 7 Hz, 2H, CH_2) 2.26, 2.88 (2m, 2 × CH_2, CH_2−P), 7.19−7.54 (m, 20H, Ph). ^{13}C NMR (C_6D_6): δ 10.05 (s, C_5Me_5), 14.08, 22.30, 31.15, 39.26 (4s, Bu), 29.41−30.20 (m, CH_2−P), 77.45, 124.45, 160.81 (3s, C), 95.40 (s, C_5Me_5), 117.44, 117.57 (2s, CN), 127.74−138.37 (Ph), 198.31 (m, Ru−C). ^{31}P NMR: δ 82.4 (s, dppe). ES-MS (m/z): 635, $[Ru(dppe)Cp^*]^+$; 792, M^+; 815, $[M + Na]^+$; 1427, $[M + Ru(dppe)Cp^*]^+$; 1607, $[2\ M + Na]^+$.

(ii) To a stirred solution of $Ru(C{\equiv}CH)(dppe)Cp^*$ (50 mg, 0.08 mmol) in thf (12 mL) at −78 °C was added BuLi (2.5 M in hexane, 45 μL, 0.11 mmol). After 40 min $Ru\{C{\equiv}CC(CN){=}C(CN)_2\}(dppe)Cp^*$ (64 mg, 0.08 mmol) was added to the solution. The solution gradually changed from deep purple to yellow-purple. Solvent was removed, and the residue was purified by preparative TLC (acetone/hexane, 3/7) to afford some starting material and bright orange $Ru\{C{\equiv}CCBu{=}C(CN)_2\}(dppe)Cp^*$ (**2**; 13 mg, 22%).

(b). R = Me (3). A stirred solution of **1** (60 mg, 0.079 mmol) in thf (10 mL) was cooled to −78 °C and treated with LiMe·LiBr (1.5 M in hexane, 60 μL, 0.09 mmol). The solution acquired an orange tinge, and a further 1 equiv of MeLi·LiBr solution (75 μL) was added, upon which the solution turned orange. The solution was warmed to room temperature, and solvent was removed. The residue was purified by preparative TLC (acetone/hexane, 3/7), an orange band (R_f = 0.44) affording bright orange $Ru\{C{\equiv}CC(Me){=}C(CN)_2\}(dppe)Cp^*$ (**3**; 45 mg, 76%). X-ray-quality crystals were grown from $CDCl_3$/MeOH or CH_2Cl_2/hexane. Anal. Calcd ($C_{43}H_{42}N_2P_2Ru$): C, 68.78; H, 5.64; N, 3.73; M_r, 750. Found: C, 68.87; H, 5.63; N, 3.74. IR/cm^{-1}: ν(C≡N) 2212 w, 2196 w, ν(C≡C) 1993 vs, ν(C=C) 1487 m, 1435 w. ^{1}H NMR: δ 1.56 (s, 15H, Cp*), 1.75 (s, 3H, Me), 2.19, 2.84 (2m, 2 × 2H, CH_2−P), 7.17−7.58 (m, 20H, Ph). ^{13}C NMR: δ 10.18 (s, C_5Me_5), 25.77 (s, Me), 28.88−30.02 (m, CH_2−P), 73.56, 124.83, 155.79 (3s, C), 95.51 (s, C_5Me_5), 117.16, 117.38 (2s, CN), 127.86−136.92 (Ph), 199.20 (m, Ru−C). ^{31}P NMR: δ 81.6 (s, dppe). ES-MS (m/z): 750, M^+; 773, $[M + Na]^+$.

(c). R = Bu^t (4). A stirred solution of **1** (81 mg, 0.106 mmol) in thf (12 mL) was cooled to −78 °C. To the solution was added LiBu^t (1.6 M solution in pentane, 80 μL, 0.128 mmol) to give an instant color change to orange. The solution was warmed to room temperature, solvent was removed, and the residue was purified by preparative TLC (acetone/hexane, 3/7) to give an orange band (R_f = 0.48) containing $Ru\{C{\equiv}CCBu^t{=}C(CN)_2\}(dppe)Cp^*$ (**4**; 23 mg, 27%). X-ray-quality crystals were grown from CH_2Cl_2/MeOH. Anal. Calcd

dx.doi.org/10.1021/om300059q | Organometallics 2012, 31, 4174−4181

($C_{46}H_{48}N_2P_2Ru$): C, 69.77; H, 6.11; N, 3.54; M_r, 792. Found: C, 69.69; H, 6.14; N, 3.66. IR/cm^{-1}: ν(CN) 2204 w, 2190 (sh), ν(C≡C) 1980 vs, ν(C═C) 1456 m, 1437 m. ^{1}H NMR: δ 0.88 (s, 9H, Bu^t), 1.55 (s, 15H, Cp*), 2.35, 2.89 (2m, 2 × 2H, CH_2–P), 7.17–7.59 (m, 20H, Ph). ^{13}C NMR: δ 10.22 (s, C_5Me_5), 29.66 (s, CMe_3), 28.50–31.02 (m, CH_2–P), 39.46 (s, CMe_3), 73.40, 125.59, 167.92 (3s, C), 95.61 (s, C_5Me_5), 118.74, 118.94 (2s, CN), 127.66–138.98 (Ph), 200.28 (m, Ru–*C*). ^{31}P NMR: δ 84.6 (s, dppe). ES-MS (*m*/*z*): 792, M$^+$.

*(d). R = Pr^i (**5**).* MgClPr^i (0.5 M solution in thf, 41 μL, 0.081 mmol) was added to a solution of **1** (41 mg, 0.054 mmol) in thf (7 mL) at 0 °C, resulting in an instant color change to orange. After the mixture was warmed to room temperature, solvent was removed and the residue was purified by preparative TLC (acetone/hexane, 3/7) to give an orange band (R_f = 0.48) containing Ru{C≡CCPr^i=C(CN)$_2$}(dppe)Cp* (**5**; 20 mg, 48%). Anal. Calcd $C_{45}H_{46}N_2P_2Ru$): C, 69.48; H, 5.96; N, 3.60; M_r, 778. Found: C, 69.62; H, 6.07; N, 3.66. IR/cm^{-1}: ν(C≡N) 2211 w, 2197 w, ν(C≡C) 1987 vs, ν(C═C) 1480 m, 1435 w. ^{1}H NMR: δ 0.68 (d, *J* = 6.6 Hz, 6H, 2 × Me), 1.55 (s, 15H, Cp*), 2.30, 2.95 (2m, 2 × 2H, CH_2–P), 2.77 (sept, *J* = 6.6 Hz, 1H, C*H*Me$_2$), 7.15–7.58 (m, 20H, Ph). ^{13}C NMR: δ 10.26 (s, C_5Me_5), 21.64 (s, Me), 29.47–31.08 (m, CH_2–P), 36.54 (s, CH), 73.20, 121.39, 165.94 (3s, C), 95.45 (s, C_5Me_5), 117.40, 117.48 (2s, CN), 127.65–138.72 (Ph), 197.90 (m, Ru–*C*). ^{31}P NMR: δ 83.7 (s, dppe). ES-MS (*m*/*z*): 801, [M + Na]$^+$.

*(e). R = CH$_2$C$_6$H$_3$Me$_2$-3,5 (**6**).* MgBr(mes) (1.0 M solution in Et$_2$O, 80 μL 0.08 mmol) was added to a solution of **1** (40 mg, 0.053 mmol) in thf (7 mL) at 0 °C. After 24 h at room temperature, solvent was removed and purification of the residue by preparative TLC (acetone/hexane, 3/7) afforded Ru{C≡CC(CH$_2$C$_6$H$_3$Me$_2$-3,5)═C(CN)$_2$}(dppe)Cp* (**6**; 5 mg, 11%) contained in an orange band (R_f = 0.48). X-ray-quality crystals were grown from CH_2Cl_2/hexane. Anal. Calcd ($C_{51}H_{50}N_2P_2Ru$): C, 71.73; H, 5.90; N, 3.28; M_r, 854. Found: C, 71.51; H, 6.65; N, 3.10. IR/cm^{-1}: ν(CN) 2209 w, ν(C≡C) 1990 vs, ν(C═C) 1485 m, 1433 w, 1420 w. ^{1}H NMR: δ 1.26 (s, 6H, 2 × Me), 1.50 (s, 15H, Cp*), 1.93, 2.33 (2m, 2 × 2H, CH_2–P), 3.21 (s, 2H, CH_2), 6.39, 6.76 (2s, 2H + 1H, *o*- and *p*-C_6H_3), 7.12–7.45 (m, 20H, Ph). ^{13}C NMR: δ 9.90 (s, C_5Me_5), 22.68 (s, $Me_2C_6H_3$), 29.21–29.69 (m, CH_2–P), 44.24 (s, C–CH_2–C_6), 75.18, 124.84, 157.00 (3s, C), 95.23 (s, C_5Me_5), 116.98, 117.57 (2s, CN), 126.57–137.55 (Ph + C_6H_3), 199.47 (m, Ru–*C*). ^{31}P NMR: δ 81.6 (s, dppe). ES-MS (*m*/*z*): 877, [M + Na]$^+$.

*(f). R = NHR′ (R′ = H (**7**), Et (**8**)).* A solution of **1** (25 mg, 0.033 mmol) in NHEt$_2$ was stirred at room temperature for 5 days, after which time the color had changed to golden yellow. Solvent was removed, and the residue was purified by preparative TLC (CH_2Cl_2/hexane, 9/1) to give two yellow compounds identified as Ru{C≡CC(NHEt)═C(CN)$_2$}(dppe)Cp* (**7**; 6 mg, 23%, R_f = 0.5) and Ru{C≡CC(NEt$_2$)═C(CN)$_2$}(dppe)Cp* (**8**; 9 mg, 34%, R_f = 0.4).

Crystals of **7** suitable for X-ray diffraction were grown from hexane.

Ru{C≡CC(NHEt)═C(CN)$_2$}(dppe)Cp (**7**).* Anal. Calcd ($C_{44}H_{45}N_3P_2Ru$): C, 67.85; H, 5.82; N, 5.40; M_r, 779. Found: C, 68.13; H, 5.90; N, 5.52. IR/cm^{-1}: ν(NH) 3394 w, ν(C≡N) 2202 w, 2175 w, ν(C≡C) 2019 vs, ν(C═C) 1542 m, 1436 w, 1421 w. ^{1}H NMR: δ 0.73 (t, *J* = 7.5 Hz, NCH$_2$*Me*), 1.56 (s, 15H, Cp*), 2.30, 2.75 (2m, 2 × CH_2, CH_2–P), 2.75 (m, CH_2, NEt), 5.36 (m, N*H*Et), 7.19–7.59 (m, 20H, Ph). ^{13}C NMR: δ 10.01 (s, C_5Me_5), 15.13 (s, CH_3, NEt), 29.34–29.95 (m, CH_2–P), 39.17 (s, CH_2, NEt), 48.32, 105.12, 151.04 (3s, C), 94.54 (s, C_5Me_5), 118.56, 119.25 (2s, CN), 127.56–138.06 (Ph), 178.84 (t, *J*(CP) = 22 Hz, Ru–*C*). ^{31}P NMR: δ 82.9 (s, dppe). ES-MS (*m*/*z*): 635, [Ru(dppe)Cp*]$^+$; 802, [M + Na]$^+$.

Ru{C≡CC(NEt$_2$)═C(CN)$_2$}(dppe)Cp (**8**).* Anal. Calcd ($C_{46}H_{49}N_3P_2Ru$): C, 68.47; H, 6.12; N, 5.21; M_r, 807. Found: C, 68.69; H, 6.43; N, 5.20. IR/cm^{-1}: ν(C≡N) 2197 w, 2170 w, ν(C≡C) 2014 s, ν(C═C) 1510 w, 1435 w, 1404 m. ^{1}H NMR: δ 0.88 (t, *J* = 7.1 Hz, 2 × Me, NEt), 1.55 (s, 15H, Cp*), 2.25, 2.84 (2m, 2 × 2H, CH_2–P), 3.25 (q, *J* = 7.1 Hz, 2 × CH_2, NEt), 7.16–7.64 (m, 20H, Ph). ^{13}C NMR: δ 10.09 (C_5Me_5), 13.58 (s, Me, NEt), 29.67–30.22 (m, CH_2–P), 45.32 (CH_2, NEt), 47.12, 108.08, 149.37 (3s, C), 94.35 (br, C_5Me_5), 120.62 (s, CN), 127.47–138.52 (Ph), 169.89 (t, *J*(CP) = 23 Hz, Ru–*C*). ^{31}P NMR: δ 83.9 (s, dppe). ES-MS (*m*/*z*): 635, [Ru(dppe)Cp*]$^+$; 808, [M + H]$^+$; 830, [M + Na]$^+$.

*(g). R = OMe (**9**).* Na (15 mg, 0.670 mmol) was dissolved in a mixture of thf and MeOH (15 mL, 2/1), and **1** (170 mg, 0.223 mmol) was added to the solution. The reaction was monitored by spot TLC, and starting material was consumed after 6 h to give a pink-red solution. Solvent was removed, and the residue was purified by column chromatography (flash silica, acetone/hexane, 3/7). The first fraction afforded Ru{C≡CC(OMe)═C(CN)$_2$}(dppe)Cp* (**9**; 61 mg, 36%) as a yellow solid. X-ray-quality crystals were obtained from $CDCl_3$/MeOH. Anal. Calcd ($C_{43}H_{42}N_2OP_2Ru$): C, 67.44; H, 5.53; N, 3.66; M_r, 766. Found: C, 67.40; H, 5.57; N, 3.70. IR/cm^{-1}: ν(C≡N) 2212 w, 2197 w, ν(C≡C) 1994 vs, ν(C═C) 1487 m, 1435 w. ^{1}H NMR: δ 1.56 (s, 15H, Cp*), 2.30, 2.78 (2m, 2 × H, CH_2–P), 3.17 (s, 3H, OMe), 7.17–7.59 (m, 20H, Ph). ^{13}C NMR: δ 10.25 (s, C_5Me_5), 29.62–30.54 (m, CH_2–P), 57.37 (s, OMe), 95.58 (s, C_5Me_5), 108.05, 159.98 (2s, C), 116.44, 117.50 (2s, CN), 128.01–137.89 (m, Ph), 192.26 (m, Ru–C). ^{31}P NMR ($CDCl_3$): δ 82.3 (s, dppe). ES-MS (*m*/*z*): 635, [Ru(dppe)Cp*]$^+$; 767, [M + H]$^+$.

*(h). R = OCH$_2$CH═CH$_2$ (**10**).* Na (23 mg, 1.00 mmol) and LiBr (17 mg, 0.197 mmol) were dissolved in a mixture of thf and allyl alcohol (9.5 mL, 16/3). **1** (75 mg, 0.099 mmol) was then added to the solution. After 2.5 h, starting material was no longer present in the now red solution. Solvent was removed, and the residue was purified by column chromatography (flash silica, acetone/hexane, 3/7), the first yellow fraction giving Ru{C≡CC(OCH$_2$CH═CH$_2$)═C(CN)$_2$}(dppe)Cp* (**10**; 32 mg, 42%) as a yellow solid. Anal. Calcd ($C_{45}H_{44}N_2OP_2Ru$): C, 68.16; H, 5.60; N, 3.54; M_r, 792. Found: C, 68.12; H, 5.71; N, 3.59. IR/cm^{-1}: ν(C≡N) 2213 m, 2199 w, ν(C≡C) 1995 vs, ν(C═C) 1487 s, 1436 m. ^{1}H NMR: δ 1.55 (s, 15H, Cp*), 2.27, 2.75 (2m, 2 × 2H, CH_2–P), 3.93 (d, *J* = 4.8 Hz, 2H, OCH_2), 4.99 (m, 1H, H_T; H_C, H_G, H_T = protons *cis*, *gem*, *trans* to OCH_2), 5.27 (m, 1H, H_C), 5.44 (m, 1H, H_G), 7.16–7.59 (m, 20H, Ph). ^{13}C NMR: δ 10.22 (s, C_5Me_5), 29.56–30.31 (m, CH_2–P), 58.48, 107.99, 158.82 (3s, C), 70.41 (s, OCH_2), 95.51 (s, C_5Me_5), 116.30, 117.51 (2s, CN), 117.37 (=CH_2), 128.13–137.65 (Ph), 191.64 (t, *J*(CP) = 23 Hz, Ru–*C*). ^{31}P NMR: δ 82.4 (s, dppe). ES-MS (*m*/*z*) 635, [Ru(dppe)Cp*]$^+$; 815, [M + Na]$^+$; 1607, [2 M + Na]$^+$.

*(i). R = OBu^t (**11**).* KOBu^t (37 mg, 0.329 mmol) was added to a solution of **1** (47 mg, 0.062 mmol) and LiCl (14 mg, 0.329 mmol) in thf (8 mL). After 30 min, solvent was removed and the residue was purified on a column of flash silica (acetone/hexane, 3/7) to give a bright yellow fraction containing Ru{C≡CC(OBu^t)═C(CN)$_2$}(dppe)Cp* (**11**; 27 mg, 54%). Anal. Calcd ($C_{46}H_{48}N_2OP_2Ru$): C, 68.39; H, 5.99; N, 3.47; M_r, 808. Found: C, 67.18; H, 6.42; N, 3.16. IR/cm^{-1}: ν(CN) 2211 w, 2196 w, ν(C≡C) 1982 vs, ν(C═C) 1489 m, 1449 w, 1438 w. ^{1}H NMR: δ 1.11 (s, 9H, Bu^t), 1.55 (s, 15H, Cp*), 2.35, 2.91 (2m, 2 × 2H, CH_2–P), 7.14–7.65 (m, 20H, Ph). ^{13}C NMR: δ 10.34 (s, C_5Me_5), 28.31 (s, $OCMe_3$), 29.08–30.82 (m, CH_2–P), 63.16, 111.89, 158.04 (3s, C), 83.24 (s, $OCMe_3$), 95.49 (s, C_5Me_5), 117.21, 117.83 (2s, CN), 127.94–138.85 (Ph), 187.49 (m, Ru-*C*). ^{31}P NMR: δ 84.5 (s, dppe). ES-MS (*m*/*z*): 831, [M + Na]$^+$.

*(j). R = OEt (**12**).* A solution of ethyl propiolate (193 mg, 1.97 mmol) in thf (10 mL) was treated with Na[N(SiMe$_3$)$_2$] (1.96 mL of 1.0 M solution in toluene, 1.97 mmol) at −78 °C. After the mixture was stirred for 30 min, **1** (100 mg, 0.131 mmol) was added, and the mixture was slowly warmed to room temperature over 8 h. Solvent was removed, and the residue was purified by column chromatography (acetone/hexane, 3/7). The first yellow fraction contained Ru{C≡CC(OEt)═C(CN)$_2$}(dppe)Cp* (**12**; 33 mg, 32%). Anal. Calcd ($C_{44}H_{44}N_2OP_2Ru$): C, 67.77; H, 5.69; N, 3.59; M_r, 780. Found: C, 67.32; H, 5.68; N, 3.57. IR/cm^{-1}: ν(CN) 2211 w, 2195 w, ν(C≡C) 1995 vs, ν(C═C) 1485 s, 1436 w. ^{1}H NMR (C_6D_6): δ 0.67 (t, *J* = 7.2 Hz, 3H, OCH_2*Me*), 1.50 (s, 15H, Cp*), 2.00, 2.72 (2m, 2 × CH_2, dppe), 3.42 (q, *J* = 7.2 Hz, 2H, O*CH*$_2$Me), 7.02–7.62 (m, 20H, Ph). ^{13}C NMR ($CDCl_3$): δ 10.20 (s, C_5Me_5), 14.82, 66.30 (2s, OEt), 29.57–30.48 (m, dppe), 95.43 (s, C_5Me_5), 107.94, 159.27 (2s, C), 116.47, 117.61 (2s, CN), 127.94–137.92 (m, Ph), 189.89 (t, *J*(CP) = 22 Hz, Ru–C). ^{31}P NMR (C_6D_6): δ 82.5 (s, dppe). ES-MS (*m*/*z*): 781, [M + H]$^+$; 803, [M + Na]$^+$; 1583, [2 M + Na]$^+$.

dx.doi.org/10.1021/om300059q | *Organometallics* 2012, 31, 4174–4181

Table 3. Crystal Data and Refinement Details

	2	3	4[a]
formula	$C_{46}H_{48}N_2P_2Ru$	$C_{43}H_{42}N_2P_2Ru$	$C_{46}H_{48}N_2P_2Ru.\ CH_4O$
mol wt	791.87	749.80	823.92
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a/Å	13.081(3)	24.1070(3)	12.9749(1)
b/Å	16.335(3)	15.5408(1)	16.3939(1)
c/Å	18.677(4)	21.5254(3)	19.8075(2)
α/deg	97.080(3)		
β/deg	94.993(4)	112.974(2)	100.480(1)
γ/deg	98.620(3)		
V/Å^3	3893	7425	4143
ρ_c/g cm^{-3}	1.35_1	1.34_2	1.32_1
Z	4	8	4
$2\theta_{max}$/deg	58	72	128
μ(Mo Kα)/mm^{-1}	0.52	0.54	4.1 [μ(Cu Kα)]
$T_{min/max}$	0.86	0.90	0.71
crystal dimens/mm^3	0.63 × 0.43 × 0.06	0.43 × 0.21 × 0.06	0.20 × 0.11 × 0.015
N_{tot}	40 918	170 886	19 286
N (R_{int})	17 648 (0.054)	34 131 (0.053)	6410 (0.032)
N_o	11 119	19 311	4926
R1	0.063	0.037	0.035
wR2 (a, b)	0.18 (0.036, 26)	0.091 (0.040, −)	0.099 (0.060, −)
T/K	150	100	100

	6	7	13	14
formula	$C_{51}H_{50}N_2P_2Ru$	$C_{44}H_{45}N_3P_2Ru$	$C_{54}H_{49}N_2OP_3Ru.\ CH_2Cl_2$	$C_{42}H_{40}N_2P_2Ru$
mol wt	853.94	778.84	1020.86	735.77
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a/Å	11.5378(3)	23.5091(8)	13.8361(3)	12.2366(7)
b/Å	15.8074(4)	16.3084(6)	14.1441(3)	15.1830(8)
c/Å	23.9009(6)	21.2864(9)	26.9670(4)	19.613(2)
α/deg			90.796(2)	
β/deg	101.215(3)	112.715(4)	104.115(2)	96.766(6)
γ/deg			108.390(2)	
V/Å^3	4276	7528	4833	3618
ρ_c/g cm^{-3}	1.32_7	1.37_4	1.40_3	1.35_1
Z	4	8	4	4
$2\theta_{max}$/deg	68	60	66	63
μ(Mo Kα)/mm^{-1}	0.48	0.54	0.58	0.55
$T_{min/max}$	0.94	0.96	0.93	0.95
crystal dimens/mm^3	0.37 × 0.12 × 0.12	0.17 × 0.08 × 0.04	0.43 × 0.17 × 0.14	0.34 × 0.30 × 0.12
N_{tot}	71 342	85 845	78 310	60 803
N (R_{int})	16 791 (0.045)	20 429 (0.10)	34 287 (0.039)	12 854 (0.039)
N_o	8979	9910	22 613	8120
R1	0.039	0.041	0.044	0.036
wR2 (a, b)	0.096 (0.045, −)	0.073 (0.0183, −)	0.121 (0.065, −)	0.092 (0.047, −)
T/K	100	100	100	100

[a]Data measured with monochromatic Cu Kα radiation; λ = 1.541 84 Å.

*(k). R = P(O)Ph$_2$ (**13**).* To a stirred solution of **1** (60 mg, 0.079 mmol, 1 equiv) in thf (8 mL) was added 1 mL of a solution of LiPPh$_2$ (1 mL of the red solution obtained from the reaction between Li (6 mg, 0.087 mmol) and PPh$_3$ (228 mg, 0.87 mmol) in thf (10 mL) over 1 day). After 2 h, solvent was removed and the residue was purified by preparative TLC (acetone/hexane, 3/7) to give a band (R_f = 0.39) containing purple Ru{C≡CC[P(O)Ph$_2$]=C(CN)$_2$}(dppe)Cp* (**13**; 29 mg, 40%). X-ray-quality crystals were grown from CH$_2$Cl$_2$/hexane. Anal. Calcd ($C_{54}H_{49}N_2OP_3Ru.CH_2Cl_2$): C, 64.70; H, 5.04; N, 2.75; M_r (unsolvated), 936. Found: C, 65.22; H, 5.31; N, 2.80. IR/cm^{-1}: ν(C≡N) 2209 w, 2191 (sh), ν(C≡C) 1958 vs, ν(C=C) 1437 m, 1425 w; in Nujol ν(CN) 2201 m, ν(C≡C) 1948v s, ν(PO) 1195 w. ^{1}H NMR: δ 1.59 (s, 15H, Cp*), 2.12, 3.65 (2m, 2 × 2H, CH$_2$−P), 6.95−7.16 (m, 30H, Ph). ^{13}C NMR: δ 9.93 (s, C_5Me_5), 29.25−30.14 (m, CH$_2$−P), 78.46 (d, J(CP) = 20 Hz, C(CN)$_2$), 97.03 (s, C_5Me_5), 117.11 (s, CN), 118.24 (d, J(CP) = 16 Hz, C), 128.01−137.89 (Ph), 146.37 (d, J(CP) = 83 Hz, =C−P), 227.85 (m, Ru−C). ^{31}P NMR: δ 23.6 (s, 1P, P(O)Ph$_2$), 83.3 (s, 2P, dppe). ES-MS (m/z): 937, [M + H]$^+$; 959, [M + Na]$^+$; 1895, [2 M + Na]$^+$.

*(l). R = H (**14**).* (i) To a stirred solution of **1** (70 mg, 0.092 mmol) in thf (10 mL) at room temperature was added a solution of Na[Fe(CO)$_2$Cp] (0.12 M, 0.84 mL, 1.1 equiv, from {Fe(CO)$_2$Cp}$_2$ (207 mg, 0.577 mmol) and 3% Na/Hg (2.1 g) in thf (10 mL)). The reaction was monitored by spot TLC and showed that starting material

dx.doi.org/10.1021/om300059q | Organometallics 2012, 31, 4174−4181

remained after 16 h. A further 3 equiv of Na[Fe(CO)$_2$Cp] solution (2.3 mL) was added. After 1 h, all the starting material had been consumed and the solution had changed from purple to orange-brown. Solvent was removed, and the residue was purified by column chromatography (flash silica, acetone/hexane, 1/4). The first brown-red fraction contained {Fe(CO)$_2$Cp}$_2$ (15 mg, 91%). The second red-orange fraction afforded Ru{C≡CCH=C(CN)$_2$}(dppe)Cp* (**14**; 60 mg, 89%) as a dark red solid. X-ray-quality crystals were obtained from $CDCl_3$/hexane. Anal. Calcd ($C_{42}H_{40}N_2P_2Ru$): C, 68.56; H, 5.48; N, 3.80; M_r, 736. Found: C, 68.61; H, 5.53; N, 3.78. IR/cm^{-1}: ν(C≡N) 2214 w, 2199 w, ν(C≡C) 1988 vs, ν(C=C) 1509 m, 1483 w, 1435 w. ^{1}H NMR ($CDCl_3$): δ 1.56 (s, 15H, Cp*), 2.19, 2.87 (2m, 2 × CH_2, CH_2–P), 6.75 (s, 1H, C=CH), 7.20–7.53 (m, 20H, Ph), ^{13}C NMR ($CDCl_3$): δ 9.99 (s, C_5Me_5), 28.92–29.86 (m, CH_2–P), 75.30, 125.52, (2s, C), 95.66 (s, C_5Me_5), 116.32, 118.35 (2s, CN), 127.38–137.33 (Ph), 142.22 (s, CH=C), 206.95 (t, J(CP) = 20 Hz, Ru–C). ^{31}P NMR ($CDCl_3$): δ 81.0 (s, dppe). ES-MS (MeCN, m/z): 635, [Ru(dppe)Cp*]$^+$; 676, [Ru(NCMe)(dppe)Cp*]$^+$; 736, M$^+$; 759, [M + Na]$^+$; 1371, [M + Ru(dppe)(C_5Me_5)]$^+$; 1495, [2 M + Na]$^+$.

(ii) Addition of Li[BHEt$_3$] (72 μL of 1.00 M solution in thf, 0.072 mmol) to **1** (50 mg, 0.066 mmol) in thf (10 mL) at −78 °C and warming to room temperature gave an orange-red solution. Removal of solvent and chromatography (silica column, acetone/hexane, 3/7) gave **14** (22 mg, 45%), identical with the complex obtained above.

Structure Determinations. Full spheres of diffraction data were measured using CCD area-detector instrumentation. N_{tot} reflections were merged to N_{unique} (R_{int} cited) after "empirical"/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ being considered "observed"; all data were used in the full matrix least-squares refinements on F^2. Data were measured using monochromatic Mo Kα radiation; λ = 0.710 73 Å. Anisotropic displacement parameter forms were refined for the non-hydrogen atoms, with hydrogen atom treatment following a "riding" model. Reflection weights were $(\sigma^2(F_o^2) + (aP)^2 + bP)^{-1}$ ($P = (F_o^2 + 2F_c^2)/3$). Neutral atom complex scattering factors were used; computation used the SHELXL 97 program.[24] Pertinent results are given in the figures (which show non-hydrogen atoms with 50% probability amplitude displacement ellipsoids) and in Tables 2 and 3 and Table S1 (Supporting Information).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Table S1, containing selected bond parameters for **2**–**4**, **6**, **7**, **13**, and **14**, figures giving additional crystal structures, and CIF files containing crystallographic details. This material is available free of charge via the Internet at http://pubs.acs.org. Full details of the structure determinations have also been deposited with the Cambridge Crystallographic Data Centre as CCDC 705838–705844 (**2**, **14**, **4**, **6**, **3**, **7**, and **13**, respectively). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Street, Cambridge CB2 1EZ, U.K. (fax, +44 1223 336 033; e-mail, deposit@ccdc.cam.ac.uk; web, http://www.ccdc.cam.ac.uk).

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Australian Research Council. We are grateful to Johnson Matthey plc, Reading, England, for a generous loan of $RuCl_3 \cdot nH_2O$.

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