3556 *Organometallics* **2008,** *27,* 3556–3563

Reactions of Alkynyl−Ruthenium Complexes with the Ketene Dithioacetal, $(MeS)_2C{=}C(CN)_2$

David J. Armitt,[†] Michael I. Bruce,*[,†] Brian W. Skelton,[‡] and Allan H. White[‡]

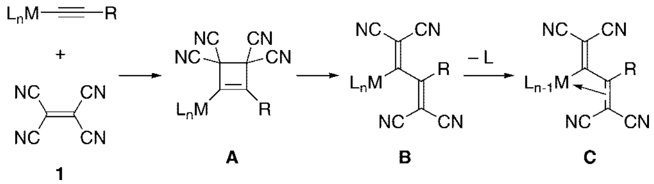
School of Chemistry and Physics, University of Adelaide, Adelaide, South Australia 5005, and
Chemistry M313, SBBCS, University of Western Australia,
Crawley, Western Australia 6009

Received November 13, 2007

Reactions of several alkynyl−ruthenium complexes with the ketene dithioacetal $(MeS)_2C{=}C(CN)_2$ (**2**) are described. The first examples of metalated 6-alkylthio-6-azafulvenes, $Ru\{C{=}CRC(SMe){=}C(CN)C{=}N(SMe)\}(PPh_3)Cp$ [R = Ph (**5a**), Fc (**5b**)], were obtained from $Ru(C{\equiv}CR)(PPh_3)_2Cp$, while $Ru(C{\equiv}CPh)(CO)(PPh_3)Cp$ gave dienyl complexes $Ru\{C(SMe){=}CPhC(SMe){=}C(CN)_2\}(CO)(PPh_3)_nCp$ [$n = 1$ (**8**), 0 (**9**)]. Yields of the azafulvenes were increased under conditions conducive to radical formation. The reaction between **5** and $Ru(C{\equiv}CC{\equiv}CPh)(PPh_3)_2Cp$ afforded the alkynyl−dienyl $Ru\{C(SMe){=}C(C{\equiv}CPh)C(SMe){=}C(CN)_2\}(PPh_3)Cp$ (**11**) and the dienynyl $Ru\{C{\equiv}CC(SMe){=}CPhC(SMe){=}C(CN)_2\}(PPh_3)_2Cp$ (**12**), formed by formal insertion of either C≡C triple bond into one C−S bond. The reaction of $Ru(C{\equiv}CPh)(PPh_3)_2Cp$ with dimethyl 2,3-dicyanofumarate (**3**) afforded diastereomers of the η^3-dienyl complex $Ru\{\eta^3\text{-}C(CN)(CO_2Me)CPhC{=}C(CN)(CO_2Me)\}(PPh_3)Cp$ (**13**). XRD structural determinations of **5a**, **8**, **9**, **11**, and one diastereomer of **13** are reported.

Introduction

Scheme 1



The reaction between tetracyanoethene (tcne, **1**) and a σ-alkynyl−transition metal complex was first described in 1979.[1] Since that time, many other reactions of this type have been studied, both by this group[2] and by others.[3–6] In general, the products arise from a formal [2 + 2]-cycloaddition leading to cyclobutenes (**A**), which can then undergo electrocyclic ring opening to give σ-1,3-butadienyl (**B**) or 1,2,3-η^3-butadienyl complexes (**C**) (Scheme 1). In some cases **A** can be isolated, and independent experiments have shown that a smooth conversion to **B** occurs more or less rapidly on warming.

While the mechanism of cyclobutene formation has not been completely elucidated, the role of the metal−ligand fragment is important. When electron-rich metal centers are present, these result in an increase in electron density and consequently the nucleophilicity of the alkynyl group. There is spectroscopic evidence of radical formation in the initial stages of the reactions of metal alkynyls, and highly colored solutions, thought to contain charge-transfer complexes, are often observed. Other electron-poor alkenes that react in this way include $(NC)_2C{=}C(CF_3)_2$[7] and $(MeO_2C)CH{=}C(CN)(CO_2Me)$,[8] the latter being used to confirm the usual electrocyclic ring-opening of the cyclobutene to butadiene. Similar [2 + 2]-cycloadditions between **1** and organic alkynes are rare, recent examples being those of *p*-(dimethylamino)phenylethynes[9] and ethynylfer-

---

* Corresponding author. Fax: + 61 8 8303 4358. E-mail: michael.bruce@adelaide.edu.au.

[†] University of Adelaide.

[‡] University of Western Australia.

(1) Davison, A.; Solar, J. P. *J. Organomet. Chem.* **1979**, *166*, C13−C16.

(2) (a) Bruce, M. I.; Hambley, T. W.; Snow, M. R.; Swincer, A. G. *Organometallics* **1985**, *4*, 494–500. (b) Bruce, M. I.; Hambley, T. W.; Snow, M. R.; Swincer, A. G. *Organometallics* **1985**, *4*, 501–508. (c) Bruce, M. I.; Duffy, D. N.; Liddell, M. J.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1987**, *335*, 365–378. (d) Bruce, M. I.; Cifuentes, M. P.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1989**, *359*, 379–399. (e) Bruce, M. I.; Ke, M.; Low, P. J.; Skelton, B. W.; White, A. H. *Organometallics* **1998**, *17*, 3539–3549. (f) Bruce, M. I.; Low, P. J.; Skelton, B. W.; White, A. H. *New J. Chem.* **1998**, *22*, 419–422. (g) Bruce, M. I.; Hall, B. C.; Kelly, B. D.; Low, P. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1999**, 3719–3728. (h) Bruce, M. I.; Smith, M. E.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **2001**, *637−639*, 484–499. (i) Bruce, M. I.; Low, P. J.; Ke, M.; Kelly, B. D.; Skelton, B. W.; Smith, M. E.; White, A. H.; Witton, N. B. *Aust. J. Chem.* **2001**, *54*, 453–460. (j) Bruce, M. I.; Low, P. J.; Hartl, F.; Humphrey, P. A.; de Montigny, F.; Jevric, M.; Lapinte, C.; Perkins, G. J.; Roberts, R. L.; Skelton, B. W.; White, A. H. *Organometallics* **2005**, *24*, 5241–5255.

(3) Kergoat, R.; Kubicki, M. M.; Comes de Lima, L. C.; Scordia, H.; Guerchais, J. E.; L'Haridon, P. *J. Organomet. Chem.* **1989**, *367*, 143–160.

(4) Cambridge, J.; Choudhary, A.; Friend, J.; Garg, R.; Hill, G.; Hussain, Z. I.; Lovett, S. M.; Whiteley, M. W. *J. Organomet. Chem.* **1999**, *577*, 249–256.

(5) Onitsuka, K.; Ose, N.; Ozawa, F.; Takahashi, S. *J. Organomet. Chem.* **1999**, *578*, 169–177.

(6) Cordiner, R. L.; Smith, M. E.; Batsanov, A. S.; Albesa-Jové, D.; Hartl, F.; Howard, J. A. K.; Low, P. J. *Inorg. Chim. Acta* **2006**, *359*, 946–961.

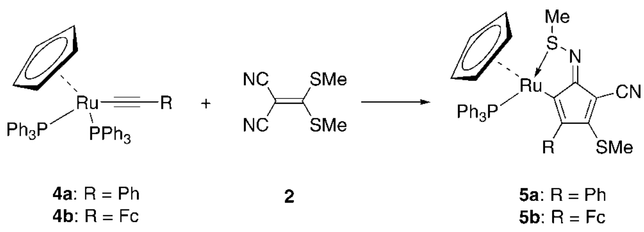
(7) (a) Bruce, M. I.; Liddell, M. J.; Snow, M. R.; Tiekink, E. R. T. *Organometallics* **1988**, *7*, 343–350. (b) Bruce, M. I.; Hambley, T. W.; Liddell, M. J.; Snow, M. R.; Swincer, A. G.; Tiekink, E. R. T. *Organometallics* **1990**, *9*, 96–104.

(8) Bruce, M. I.; Duffy, D. N.; Liddell, M. J.; Tiekink, E. R. T.; Nicholson, B. K. *Organometallics* **1992**, *11*, 1527–1536.

(9) (a) Michinobu, T.; May, J. C.; Lim, J. H.; Boudon, C.; Gisselbrecht, J.-P.; Seiler, P.; Gross, M.; Biaggio, I.; Diederich, F. *Chem. Commun.* **2005**, 737–739. (b) Michinobu, T.; Boudon, C.; Gisselbrecht, J.-P.; Seiler, P.; Frank, B.; Moonan, N. N. P.; Gross, M.; Diederich, F. *Chem.−Eur. J.* **2006**, *12*, 1889–1905.

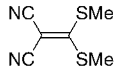
10.1021/om7011437 CCC: $40.75

Scheme 2

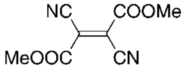


rocenes;[10] tetrathiofulvene has also been reported to enter into similar reactions.[11]

Ketene dithiodiacetals are extremely useful as synthons and have multiple reactivity, often as precursors to various heterocycles.[12] We considered that the highly polarized C=C double bond in $\mathrm{(MeS)_2C{=}C(CN)_2}$ (**2**)[13] would be an ideal coupling partner in dipolar two-step cycloaddition reactions with σ-alkynylmetal complexes, and with a view to extending the range of these reactions, we have studied some reactions of **2** with $\mathrm{Ru(C{\equiv}CPh)(PPh_3)_2Cp}$ and related complexes. A related reaction of dimethyl 2,3-dicyanofumarate (**3**) is also reported.



2



3

Results and Discussion

When a mixture of $\mathrm{Ru(C{\equiv}CPh)(PPh_3)_2Cp}$ (**4a**) with a slight excess of $\mathrm{(MeS)_2C{=}C(CN)_2}$ (**2**) was heated in refluxing benzene, the color gradually changed from yellow-orange to deep red over a period of 24 h. Column chromatography (basic alumina) gave the novel 6-methylthio-6-azafulvene complex **5a** in 26% yield after recrystallization, along with extensive recovery of the reactants (Scheme 2).

The structure of **5a**, which is the first reported complex containing this type of ligand, was determined by X-ray crystallography (Figure 1). Selected bond lengths and angles for complexes **5a**, **8**, **9**, and **11** are summarized in Table 1.

In **5a**, the ruthenium center adopts the usual pseudo-octahedral geometry, with < Ru–C(cp)> 2.24(2) and Ru–P 2.2944(4) Å and angles S(5)–Ru–P 101.19(2)°, S(5)–Ru–C(1) 80.93(4)°, and P–Ru–C(1) 91.68(4)°. The organic ligand appears to be unprecedented and chelates the metal via C(1) and S(5). The Ru–C(1) bond length [2.025(1) Å] is similar to those found in other compounds containing Ru–C(sp^2) bonds,[2] while the Ru–S bond [2.2589(4) Å] is somewhat shorter than found in other ruthenium complexes with pendant MeS ligands (2.309–2.401 Å).[14] The closest structural analogue to the organic ligand is the cyclopentadithiazole **6**, which has N(1)=C(2) and N(1)–S(2) bonds of 1.306(12) and 1.632(9) Å, respectively,[15] compared with values for C(5)–N(5) and the longer N(5)–S(5) bonds of 1.290(2) and 1.741(1) Å found for **5a**. Within the C_5 ring of **5a**, C(1)–C(2) and C(3)–C(4) are 1.378(2) and 1.377(2) Å, with values for C(2)–C(3), C(1)–C(5), and C(4–5) being 1.485(2), 1.512(2), and 1.461(2) Å, respectively [cf. analogous separations in **6**: C(1)–C(5) 1.379(14), C(3)–C(4) 1.398(14), C(4)–C(5) 1.440(14), C(1)–C(2) 1.482(13), and C(2)–C(3) 1.447(14) Å].

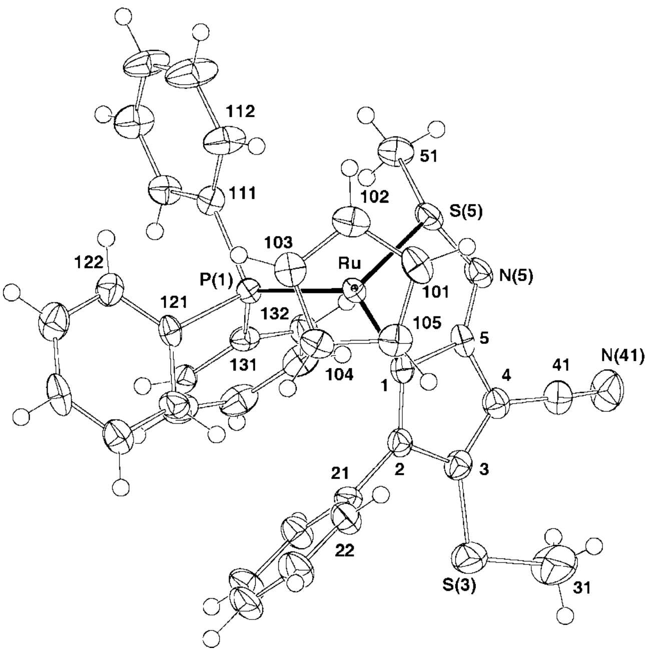
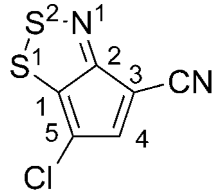


Figure 1. Plot of a molecule of $\mathrm{Ru\{C{=}CRC(SMe){=}C(CN)C{=}N(SMe)\}(PPh_3)Cp}$ (**5a**).

Spectroscopic data for **5a** are consistent with the molecular structure; a molecular ion at *m/z* 700 was observed in the electrospray mass spectrum (ES-MS), while an IR absorption band at 2192 $\mathrm{cm^{-1}}$ is assigned to ν(CN). The relative intensities of the aromatic (δ 7.29–7.46), cyclopentadienyl (δ 4.74), and methyl peaks (δ 1.65, 2.67) in the ^{1}H NMR spectrum indicated the loss of one $\mathrm{PPh_3}$ ligand from the metal center of the precursor. However, the methyl signal at δ 2.67 was very broad, possibly signifying slow dissociation and recoordination of the MeS ligand in solution on the NMR time scale at 294 K. At 323 K, the methyl signal became noticeably sharper, while a second set of phenyl, cyclopentadienyl, and methyl peaks appeared at δ 6.77–6.91, 4.46, 2.80, and 2.17 in a ca. 1:1 ratio with the original peaks, possibly due to a presently uncharacterised isomer.



6

Formally, **5a** arises from the [3 + 2]-cycloaddition of the metalated alkyne to the acrylonitrile subunit of **2**, with con-

---

[10] Mochida, T.; Yamazaki, S. *J. Chem. Soc., Dalton Trans.* **2002**, 3559–3564.

[11] Hopf, H.; Kreutzer, M.; Jones, P. G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1127–1128.

[12] (a) Borrman, D. *Houben-Weyl Methoden der Organischen Chemie*; Thieme: Stuttgart, 1968; Vol. VII/4, pp 404–441. (b) Schaumann, E. *Houben-Weyl Methoden der Organischen Chemie*; Thieme: Stuttgart, 1985; Vol. E11/4, pp 260–324. (c) Dieter, R. K. *Tetrahedron* **1986**, *42*, 3029–3096. (d) Junjappa, H.; Ila, H.; Asokan, C. V. *Tetrahedron* **1990**, *46*, 5423–5506.

[13] (a) Sandström, J.; Wannerbeck, I. *Acta Chem. Scand.* **1970**, *24*, 1191–1201. (b) Ericsson, E.; Marnung, T.; Sandström, J.; Wannerbeck, I. *J. Mol. Struct.* **1975**, *24*, 373–387. (c) Kleinpeter, E.; Klod, S.; Rudorf, W.-D. *J. Org. Chem.* **2004**, *69*, 4317–4329. (d) Kleinpeter, E.; Schulenburg, A. *Tetrahedron Lett.* **2005**, *46*, 5995–5997.

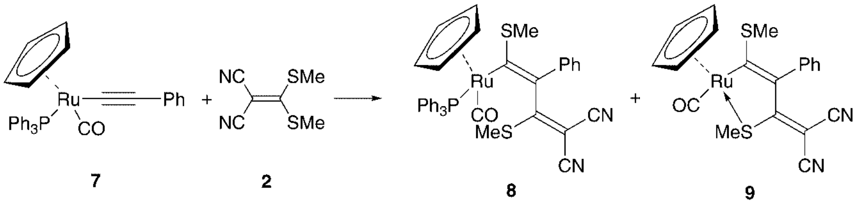
[14] (a) Hossain, M.; Maji, M.; Chattopadhyay, S. K.; Ghosh, S.; Blake, A. J. *Polyhedron* **1998**, *17*, 1897–1906. (b) Maji, M.; Hossain, M.; Chatterjee, M.; Chattopadhyay, S. K.; Puranik, V. G.; Chakrabarti, P.; Ghosh, S. *Polyhedron* **1999**, *18*, 3735–3739. (c) Moreno, M. A.; Haukka, M.; Jääskeläinen, S.; Vuoti, S.; Pursiainen, J.; Pakkanen, T. A. *J. Organomet. Chem.* **2005**, *690*, 3803–3814.

Table 1. Selected Bond Distances and Angles[a]

	5a	**8**	**9;9′**	**11**
		Bond Distances (Å)		
Ru−P/C(CO)	2.2944(4)	2.3229(4)	1.871(2); 1.865(2) [C]	2.311(3)
Ru−S/C(CO)	2.2589(4)	1.845(2) [C]	2.3132(5); 2.2881(6)	2.305(4)
Ru−C(0) (cp)	1.87_5	1.92_5	1.89_4; 1.89_6	1.88_3
Ru−C(cp)	2.222−2.266(2)	2.261−2.280(2)	2.235−2.258(2); 2.230−2.266(2)	2.219−2.247(11)
<>	2.24(2)	2.271(8)	2.246(9); 2.25(1)	2.235(12)
Ru−C(1)	2.025(1)	2.099(2)	2.058(2); 2.049(2)	1.991(9) [C(4)]
C(1)−C(2)	1.378(2)	1.387(2)	1.412(3); 1.412(2)	1.43(2)
C(1)−S(1)		1.756(2)	1.740(2); 1.732(2)	1.75(1)
C(11)−S(1)		1.813(2)	1.798(3); 1.802(2)	1.81(1)
C(2)−C(21)	1.475(2)	1.490(2)	1.498(3); 1.500(2)	1.39(1)
C(2)−C(3)	1.485(2)	1.463(2)	1.403(3); 1.403(3)	1.38(2)
C(3)−S(3)	1.721(2)	1.743(2)	1.805(2); 1.801(2)	1.815(9)
C(31)−S(3)	1.786(2)	1.794(2)	1.814(2); 1.814(2)	1.82(1)
C(3)−C(4)	1.377(2)	1.383(2)	1.399(3); 1.392(3)	1.39(2)
C(4)−C(41,42)	1.424(2), −	1.428, 1.432(3)	1.432, 1.429(3); 1.428, 1.431(3)	1.42, 1.43(2)
		Bond Angles (deg)		
C(1)−Ru−S/C(01)	80.93(4)	89.72(7)	81.44(5); 81.16(5) [S(3)]	81.8(4)
P−Ru−S	101.19(2)			89.8(1)
P−Ru−C(1)	91.68(4)	94.86(4)	91.57(8); 92.31(8)	91.3(4)
Ru−C(1)−S		109.61(6)	126.8(1); 126.42(9)	129.0(7)
C(1)−C(2)−C(3)	110.0(1)	120.3(2)	119.2(2); 118.0(1)	118.8(9)
C(1)−C(2)−C(21)	129.1(1)	125.0(1)	121.6(2); 122.3(2)	122.7(12)
C(2)−C(3)−C(4)	110.1(1)	119.6(2)	129.2(2); 130.3(2)	130.9(9)
C(2)−C(3)−S(3)	117.4(1)	124.6(1)	114.0(1); 114.0(1)	
C(3)−C(4)−C(41,42)	130.8(2), −	121.3, 122.6(2)	125.4(2), 121.0(2); 125.7(2), 120.2(2)	124.9, 123.5(12)

[a] For **5a**: C(1)−C(5) 1.512(2), C(4)−C(5) 1.461(2), C(5)−N(5) 1.290(2), C(51)−S(5) 1.806(2), N(5)−S(5) 1.741(1) Å, N(5)−S(5)−Ru 107.67(5)°, N(5)−S(5)−C(51) 96.93(7)°, S(5)−N(5)−C(5) 109.6(1)°, C(2)−C(1)−C(5) 104.4(1)°, C(1)−C(5)−C(4) 109.6(1)°, C(1)−C(5)−N(5) 125.4(1)°, C(4)−C(5)−N(5) 124.9(1)°. For **8**: P−Ru−C(01) 87.75(5)°, C(3)−S(3)−C(31) 105.27(8)°, Ru−C(1)−C(2) 131.3(1)°. For **9**; **9′**: S(3)−Ru−C(01) 96.45(6)°; 95.70(7)°, Ru−S(3)−C(3) 102.06(6)°; 101.82(6)°, C(2)−C(1)−S(1) 111.6(1)°; 112.7(1)°, C(4)−C(3)−S(3) 116.8(1)°; 115.7(1)°. For **11**: C(21)−C(22) 1.22(1), C(22)−C(23) 1.45(1) Å, C(1)−S(1)−C(11) 109.1(5)°, Ru−S(3)−C(3) 102.5(5)°, Ru−S(3)−C(31) 108.3(5)°, Ru−C(1)−C(2) 123.4(9)°, C(2)−C(1)−S(1) 107.6(7)°, C(3)−C(2)−C(21) 118.5(11)°, S(3)−C(3)−C(4) 115.8(9)°, C(2)−C(21)−C(22) 173.6(15)°, C(21)−C(22)−C(23) 176.6(14)°, S(3)−C(3)−C(2) 113.3(9)°.

Scheme 3



comitant 1,4-migration of a methylthio group. It is unlikely, however, that the reaction proceeds in a concerted fashion. While addition of the radical initiator AIBN resulted in only a modest increase in the yield of **5a** to 42%, irradiation with a broad-spectrum sun lamp gave a dramatic increase in yield to 71%. These results may implicate the participation of radical species in the mechanistic pathway leading to **5a**.

Treatment of the more electron-rich acetylide Ru(C≡CFc)$(PPh_3)_2$Cp (**4b**) with **2** resulted in the formation of the corresponding 6-azafulvene **5b** in 28% yield. The dark red product was characterized by comparison of its spectroscopic data with those of **5a**; in particular, the broadened methyl signal in its ^{1}H NMR spectrum is a useful diagnostic tool. Other spectral data include resonances for Ph (δ_H 7.16−7.33, δ_C 128.3−133.3), RuCp (δ_H 4.85, δ_C 85.4), FeCp (δ_H 4.11, δ_C 83.6), $Fe(C_5H_4)$ (δ_H 4.27, 4.44, 4.66, δ_C 69.1, 69.6, 71.5, 72.2), and PPh_3 (δ_P 48.5), with carbon chain atoms at δ_C 26.3, 29.7. The IR band at 2192 cm^{-1} is assigned to ν(CN). The ES-MS contains M^+ and $[M + Na]^+$ at *m/z* 808 and 831, respectively.

The reaction between **2** and Ru(C≡CPh)(CO)(PPh_3)Cp (**7**) takes a different course, affording the butadienyl complexes **8** and **9** in 31% and 11% yields, respectively (Scheme 3). The structures of **8** and **9** were deduced by a combination of spectroscopic and crystallographic methods.

The ES-MS of **8** contained an ion at *m/z* 751, corresponding to $[M + Na]^+$, IR absorptions were observed at 2251, 2210 [ν(CN)] and 1940 cm^{-1} [ν(CO)], and the $^{31}P\{^1H\}$ NMR spectrum confirmed the presence of the PPh_3 ligand (δ_P 50.1). The $^{13}C\{^1H\}$ NMR spectrum contained three signals between δ 112.7 and 117.1 attributed to two CN resonances and one carbon from the 1,3-butadienyl backbone. Other resonances arising from the Me (δ_H 1.50, 2.25; δ_C 17.7, 26.7), Cp (δ_H 5.18, δ_C 90.5), and phenyl groups (δ_H 7.33−7.53, δ_C 126.0−138.2) were present. The Ru−CO ligand gives a doublet at δ 204.8 [J(CP) = 20.3 Hz], while C(1) is found at δ 189.5.

The XRD molecular structure obtained from deep red, rod-like crystals of $8 \cdot CH_2Cl_2$ is shown in Figure 2. The ruthenium center has the usual distorted octahedral geometry [Ru−CO 1.845(2), Ru−P 2.3229(4), <Ru−C(cp)> 2.271(8) Å; P−Ru−C(1,01) 94.86(4), 87.75(5), C(1)−Ru−C(01) 89.72(7)°]. With four different substituents, the Ru center is chiral, and the centrosymmetric crystal contains equal amounts of both enantiomers. In the organic ligand, sequential C(1)−C(2)−C(3)−C(4) bond lengths [1.387(2), 1.463(2), 1.383(2) Å] are consistent with alternating C═C double and C−C single bonds in the butadienyl group, while the Ru−C(1) distance

---

(15) Gómez, T.; Macho, S.; Miguel, D.; Neo, A. G.; Rodríguez, T.; Torroba, T. *Eur. J. Org. Chem.* **2005**, 5055–5066.

[2.099(2) Å] lies in the range typical for an Ru−C(sp^2) bond.[2] The diene has the *s-trans* conformation found previously for most analogous complexes. An angle of 55.6° is subtended by the two halves of the 1,3-butadien-1-yl ligand, similar to those reported previously for related complexes.[2] There is also some twisting of the C(1)−C(2) double bond, as shown by the Ru−C(1)−C(2)−C(3) and S(1)−C(1)−C(2)−C(21) torsion angles of 26.4(3)° and 24.0(2)°, respectively.

The ion at *m/z* 489 observed in the ES-MS of **9** is assigned to $[M + Na]^+$ and indicates that PPh_3 is no longer present. This was confirmed by the ratio of the aromatic, cyclopentadienyl, and methyl signals in its ^1H NMR spectrum and the absence of any ^{31}P signal. As a consequence, the $^{13}C\{^1H\}$ NMR spectrum is greatly simplified, with characteristic signals for the CO ligand (δ_C 201.1), CN (δ_C 112.5, 117.6), Cp (δ_H 5.21, δ_C 86.0), and two MeS groups (δ_H 2.51, 2.83, δ_C 29.7). Resonances at δ_C 32.8, 89.5, 137.5, 144.1, and 170.5 are assigned to the carbon skeleton of the thiolate ligand. As for **8**, the IR spectrum of **9** contained absorptions at 2200 [ν(CN)] and 1953 cm^{-1} [ν(CO)].

Recrystallization of **9** from CH_2Cl_2/MeOH afforded yellow-brown crystals with two distinct morphologies, plates and rods. Samples of each were examined by X-ray crystallography (Figure 3), and it was found that the difference lay entirely in the molecular dispositions within their unit cells, both of which have the common feature of centrosymmetrically related molecular pairs in similar alignments. Comparison of the bond parameters for the two forms showed only minor differences. The following discussion therefore cites the values found for the rod form.

Coordination about the pseudo-octahedral Ru atom is achieved by the Cp [<Ru−C(cp)> 2.25(1) Å], CO [1.865(2) Å]. and the chelating vinyl-thio ligands [Ru−C(1) 2.049(2), Ru−S(3) 2.2881(6) Å; S(3)−Ru−C(1,01) 81.16(5), 95.70(7), C(1)−Ru−C(01) 92.31(8)°]. In stark contrast to **8**, an almost planar butadienyl ligand is present in **9** [internal angles at Ru−C(1)−C(2)−C(3)−S(3) are 81.16(5)°, 120.7(1)°, 118.0(1)°, 114.0(1)°, and 101.82(6)° (Σ = 535.7°)]. Extensive delocalization of the π-system is indicated by the nearly equal bond lengths along the butadienyl backbone [C(1)−C(2)−C(3)−C(4) 1.412(2), 1.403(3), 1.392(3) Å], while the coordination of the SMe group to the metal is reflected in the increased length of the C(3)−S(3) bond [1.801(2) Å].

The reaction of Ru(C≡CC≡CPh)$(PPh_3)_2$Cp (**10**) with **2** also afforded two major adducts, to which we assign structures **11** and **12**, i.e., the products of addition of **2** to each of the C≡C systems in **10** (Scheme 4).

In the case of **11**, the molecular structure has been confirmed by an XRD structure determination (Figure 4), which showed that a formal insertion of the C≡C triple bond adjacent to the metal center into one of the C−SMe bonds of **2** had occurred. The formulation is consistent with the observation of $[M + Na]^+$ at *m/z* 747 in the ES-MS and the ^1H NMR spectrum, which confirmed that only one PPh_3 ligand was present. The usual Ru(PPh_3)Cp fragment [Ru−P 2.311(3), <Ru−C(cp)> 2.235(12) Å] also bears a chelating vinyl-thiolate ligand [Ru−S(1) 2.305(4), Ru−C(4) 1.991(9) Å; S(3)−Ru-P 89.8(1)°, S−Ru−C(1) 81.8(4)°, P−Ru−C(1) 91.3(4)°] resembling that in **9**. The butadienyl ligand in **11** differs slightly from that in **9**; the somewhat shorter Ru−C(1) bond [1.991(9) **11**, cf. 2.058(2) Å in **9**] and the C(1)−C(2)−C(3) separations [1.43(2), 1.38(2) Å] suggest that electronic reorganization within the ring results in some multiple bond character in the Ru−C(1) bond, reflecting the more electron-rich metal center. Internal angles at Ru−S(3)−C(3)−C(2)−C(1) are 81.8(4)°, 102.5(5)°, 113.3(9)°, 118.8(9)°, and 123.4(9)°, respectively. Also noteworthy is the *syn*-arrangement of the angular methyl group attached to sulfur and the cyclopentadienyl ligand of the metallocycle; in compounds **5a** and **9** these groups have an *anti*-orientation. The presence of the C(21)≡C(22)−Ph fragment [C(21)−C(22) 1.22(1), C(22)−C(23) 1.45(1) Å] confirms that reaction of the cyano-ketal has occurred at the inner C≡C triple bond.

Unfortunately, crystals of **12** suitable for X-ray crystallography could not be obtained. The structural assignment is therefore based on the spectroscopic similarities between **8** and **12**, particularly in their IR spectra. The broad intense ν(C≡C) absorption at 2017 cm^{-1} is similar to that observed at 1993 cm^{-1} in Ru{C≡CC[=C(CN)$_2$]C=C(CN)$_2$}(dppe)Cp, for example, albeit shifted by 20−30 cm^{-1} to higher frequency;[2f,g]

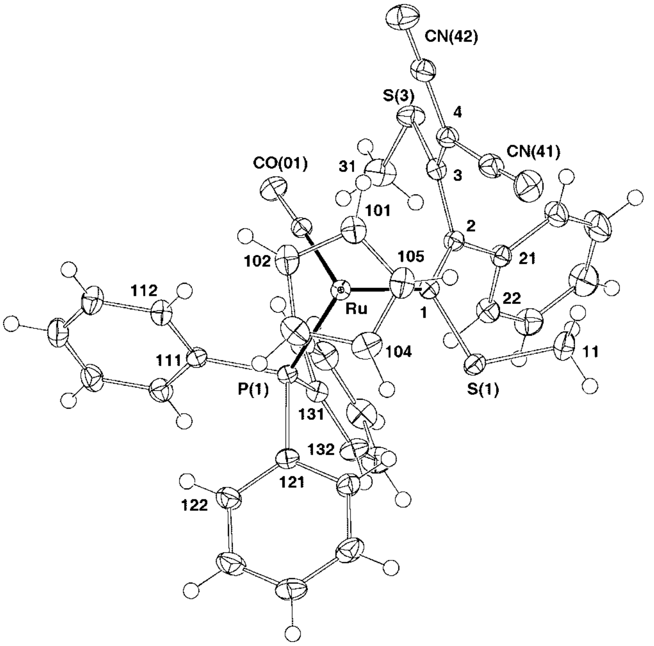


Figure 2. Plot of a molecule of Ru{C(SMe)=CPhC(SMe)=C(CN)$_2$}(CO)(PPh_3)Cp (**8**).

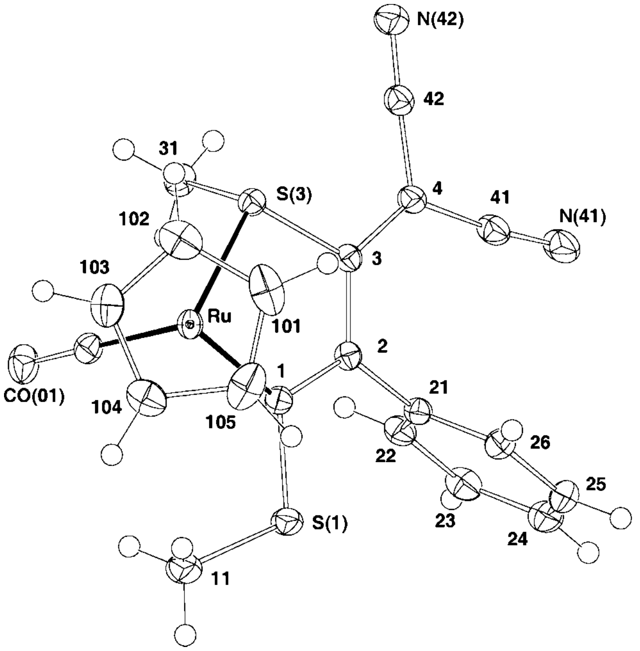
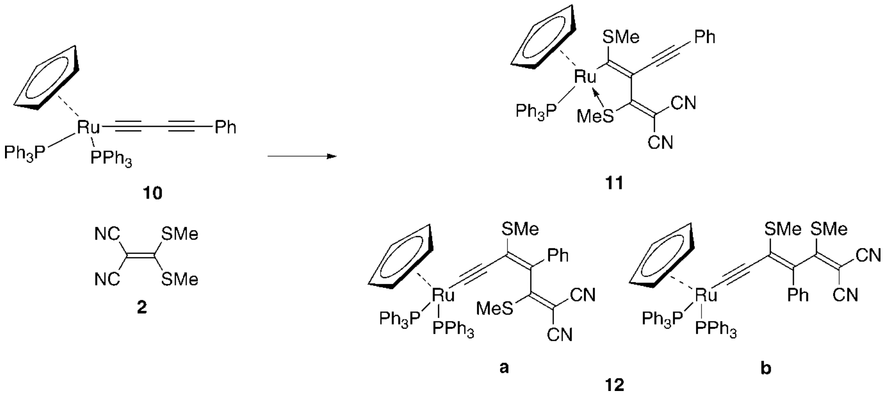


Figure 3. Plot of a molecule of Ru{C(SMe)=CPhC(SMe)=C(CN)$_2$}(CO)Cp (**9**).

Scheme 4



in comparison, the $\nu(C\equiv C)$ absorptions for organic alkynes generally lie between 2100 and 2200 cm^{-1}. Ions at *m/z* 1009 and 987 in the ES-MS correspond to $[M + Na]^+$ and $[M + H]^+$, respectively, and confirm the retention of both phosphine ligands in this derivative. The NMR spectra of **12** contain two sets of signals of relative intensities 3:2, although it is not clear whether these result from the presence of two inseparable isomeric forms (e.g., **12a** and **12b**) or from two rotamers. Thus, resonances for the Me (δ_H 1.73 and 2.237, δ_C 15.9 and 29.7) and Cp (δ_H 4.46, δ_C 86.4) for the major isomer are accompanied by others at δ_H 2.19, 2.242, δ_C 16.7 (Me), and δ_H 4.33, δ_C 86.1 (Cp) from the minor component. The relatively large difference in the Me chemical shifts suggests that one Me group of the major component lies in close proximity to an aromatic ring, most likely that of a PPh_3 ligand.

The formation of compounds **8**, **9**, **11**, and **12** occurs via a formal *trans*-insertion of the alkynyl or butadiynyl ligand of **4a** into one carbon−sulfur bond of the ketene dithioacetal. To date, there have been very few reported examples of insertions of alkynes into carbon−sulfur bonds of any type,[16] the majority involving reactions of the coordinated bond of η^2-complexes of carbon disulfide or dithioformate with electron-deficient alkynes. There are also examples of additions of metal thiolates to alkynes to give complexes with structures similar to those found in **9** and **11**.[2b,17]

In general, most mechanisms accounting for the insertion of unsaturated hydrocarbons into σ-bonds invoke a *cis*-addition process, even when exclusively *trans*-adducts, or mixtures of *cis* and *trans* isomers, are obtained.[18] Thus it is likely that the insertion reactions observed here also follow a *cis*-addition pathway. We suggest that the polar C=C double bond of the ketene dithioacetal and the nucleophilic alkynyl C_β atom (and by extension, the δ-position of butadiynyl ligands)[19] initially form zwitterionic intermediate **D** (Scheme 5), which then undergoes a 1,3-shift of a methylthio group, in a process that may be either concerted or stepwise.[20] The *trans*-adduct **E** (cf. **8**, R = Ph) may thus be formed directly, or via an intermediate *cis*-adduct **F** followed by isomerization. Loss of PPh_3 or CO from **E** then gives **9** or **11**, respectively.

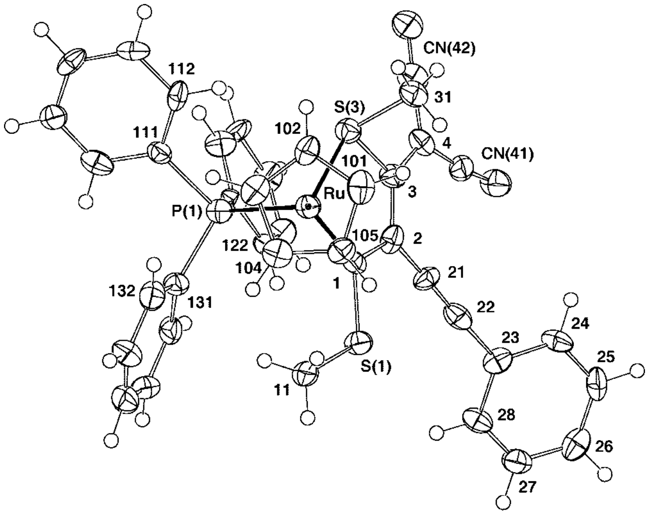


Figure 4. Plot of a molecule of Ru{C(SMe)=CC≡CPh)C(SMe)=C(CN)₂}(PPh₃)Cp (**11**).

Triphenylphosphine liberated during the reaction could catalyze the isomerization; alternatively, it is possible that ambient light promotes biradical formation in which both radical centers are further stabilized by delocalization. Such a relatively long-lived radical species may undergo internal rotation prior to recombination, as established for stilbenes, to form **E**. On the other hand, intramolecular addition of the α-carbon-centered radical to a nitrile group might give a 6-azafulvene biradical as an advanced intermediate in the formation of **5**, although no products of type **E** were detected during the reactions leading to **5**.

Reaction of Ru(C≡CPh)(PPh₃)₂Cp with Dimethyl Dicyanofumarate. Treatment of **4a** with dimethyl dicyanofumarate (**3**) under the same conditions described for the cycloaddition of **1** afforded the 1,2,3-η^3-butadienyl complex **13** in 21% yield (Scheme 6). The reaction mixture became deep claret, then intense violet after a few minutes, possibly as a result of the formation of an intermediate charge-transfer complex(es). Complex **13**, obtained as an orange solid, was characterized as

---

(16) Bruce, M. I.; Swincer, A. G. *Aust. J. Chem.* **1980**, *33*, 1471–1483.

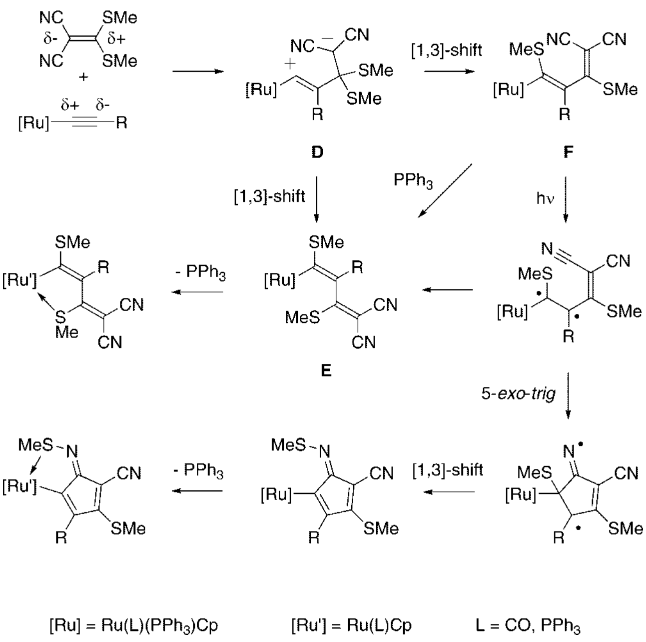
(17) (a) Kubicki, M. M.; Kergoat, R.; Scordia, H.; Gomes de Lima, L. C.; Guerchais, J. E.; L'Haridon, P. *J. Organomet. Chem.* **1988**, *340*, 41–49. (b) Petillon, F. Y.; Le Floch-Perennou, F.; Guerchais, J. E.; Sharp, D. W. A. *J. Organomet. Chem.* **1979**, *173*, 89–106. (c) Guerchais, J. E.; Le Floch-Perennou, F.; Petillon, F. Y.; Keith, A. N.; Manojlovic-Muir, L.; Muir, K. W.; Sharp, D. W. A. *J. Chem. Soc., Chem. Commun.* **1979**, 410–411.

(18) Cross, R. J.; Davidson, M. F. *J. Chem. Soc., Dalton Trans.* **1986**, 411–414.

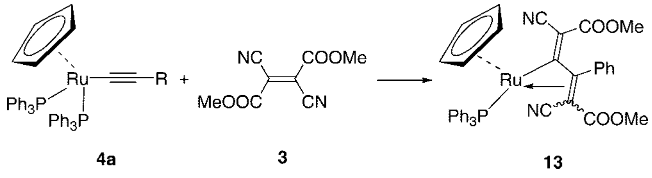
(19) (a) Le Bozec, H.; Gorgues, A.; Dixneuf, P. H. *Inorg. Chem.* **1981**, *20*, 2486–2489. (b) Touchard, D.; Dixneuf, P. H.; Adams, R. A.; Segmüller, B. E. *Organometallics* **1984**, *3*, 640–642. (c) Fischer, H.; Gerbing, U.; Tiriliomis, A. *J. Organomet. Chem.* **1987**, *332*, 105–114. (d) Fischer, H.; Hofmann, J.; Gerbing, U.; Tiriliomis, A. *J. Organomet. Chem.* **1988**, *358*, 229–244. (e) Touchard, D.; Fillaut, J.-L.; Dixneuf, P. H.; Adams, R. A.; Segmüller, B. E. *J. Organomet. Chem.* **1990**, *386*, 95–109. (f) Khasnis, D. V.; Pirio, N.; Touchard, D.; Toupet, L.; Dixneuf, P. H. *Inorg. Chim. Acta* **1992**, *198−200*, 193–201. (g) Hogarth, G.; Skordalakis, E. *J. Organomet. Chem.* **1993**, *458*, C8−C9. (h) Forster, G. D.; Hogarth, G. *J. Chem. Soc., Dalton Trans.* **1997**, 2305–2307.

(20) Davidson, J. L.; Shiralian, M.; Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1984**, 2167–2176.

Scheme 5



Scheme 6



the 1:1 adduct by NMR, IR, ES-MS, and elemental analysis and contains only one PPh$_3$ ligand, while the presence of two ν(CN) (2250, 2212 cm^{-1}) and two ν(ester CO) absorptions (1715, 1615 cm^{-1}) in the IR spectrum is consistent with the desymmetrization of the original alkene unit.

The NMR spectra of **13** contain two sets of resonances, with intensity ratio approximately 3:2, indicating the presence of two isomers. At this time it is not clear whether this is a consequence of differing orientations of **3** with respect to the metal acetylide during the presumed initial cycloaddition step, of isomerization of the reactant **3** (unlikely), or of internal rotation of an intermediate zwitterion or biradical adduct. The XRD structure determination of **13** shows that only one enantiomer is present in the unit cell, along with its mirror image; however, NMR analysis of a recrystallized sample again showed the same ratio of isomers, making it impossible to determine if the structure obtained was the minor or major enantiomer. The molecular structure of **13** (Figure 5) is similar to those of other η^3-dienyl complexes **14**,[2j] **15**,[21] and **16** (Chart 1).[8]

The Ru(PPh$_3$)Cp fragment [Ru−P 2.3785(7), <Ru−C(cp)> 2.22(2) Å] is bonded to the η^3-dienyl ligand [Ru−C(2,3,4) 2.218, 2.128, 1.998(3) Å; P−Ru−C(2) 98.12(7)°], which bears CN and CO$_2$Me substituents on C(2), Ph on C(3), and =C(CN)(CO$_2$Me) on C(4). Overall, this ligand is similar to several others that have been obtained from addition of electron-deficient alkenes to alkynyl−metal complexes containing an easily displaceable ligand.[2]

Conclusions

The reactions of transition metal alkynyls with the ketene *S,S*-diacetal **2** have given novel metalated 6-alkylthio-6-azafulvenes **5** or 1,3-butadien-1-yl complexes **8**, **9**, **11**, and **12**, depending on the nature of metal alkynyl. Increases in yields found under appropriate conditions suggest the involvement of radical species. The presence of two different labile ligands in complexes **5** may result in useful catalytic activity, particularly if one of the ligands is tethered. A further example of an η^3-butadienyl complex (**13**) was obtained in low yield from the reaction between Ru(C≡CPh)(PPh$_3$)$_2$Cp and dimethyl dicyanofumarate.

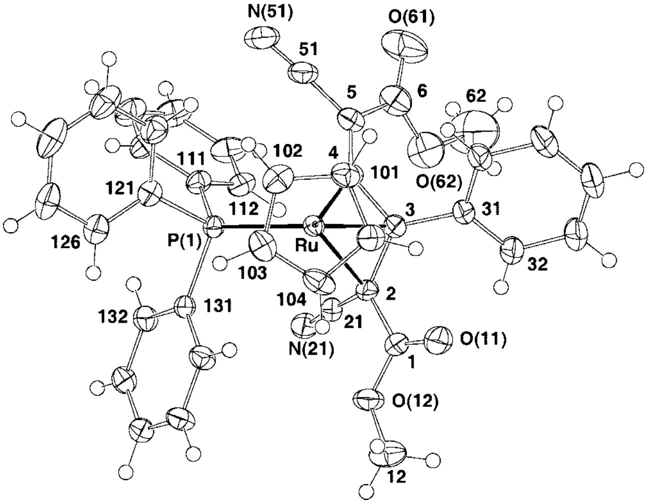
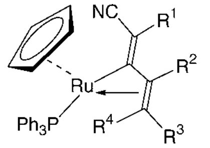


Figure 5. Plot of a molecule of Ru{η^3-C(CN)(CO$_2$Me)-CPhC=C(CN)(CO$_2$Me)}(PPh$_3$)Cp (**13**). Selected bond distances (Å) and angles (deg): Ru−P 2.3785(7), <Ru−C(cp)> 2.22(2), centroid 1.87, Ru−C(2,3,4) 2.218(3), 2.128(3), 1.998(3), C(2)−C(3) 1.458(4), C(3)−C(4) 1.430(4), C(4)−C(5) 1.347(5); P−Ru−C(2) 98.12(7), P−Ru−C(3) 114.06(8), P−Ru−C(4) 89.02(8), C(cp centroid)−Ru−C(2,3,4) are: 128.4, 126.5, 137.5, C(2)−C(3)−C(4) 115.1(2), C(3)−C(4)−C(5) 136.2(3).

Chart 1



	R^1	R^2	R^3	R^4
14	CN	Fc	CN	CN
15	CN	Ph	CF$_3$	CF$_3$
16	CO$_2$Me	Ph	CO$_2$Me	H

Experimental Section

General Procedures. All reactions were performed in oven-dried glassware under a dry N$_2$ atmosphere, although normally no special precautions to exclude air were taken during subsequent workup. Common solvents were dried, distilled under argon, and degassed with a stream of dry N$_2$ before use; CH$_2$Cl$_2$ was distilled from CaH$_2$ prior to use, and benzene was used as supplied. 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).

Instruments. IR spectra were obtained on a Bruker IFS28 FT-IR spectrometer. Spectra in CH$_2$Cl$_2$ were obtained using a 0.5 mm path-length solution cell with NaCl windows. Nujol mull spectra were obtained from samples mounted between NaCl discs. NMR spectra were recorded on a Varian 2000 instrument (^{1}H at 300.13 MHz, ^{13}C at 75.47 MHz, ^{31}P at 121.503 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$_3$PO$_4$ for ^{31}P NMR spectra. Electrospray mass spectra in positive-ion mode (ES-MS) were obtained from samples dissolved in MeOH unless otherwise

---

[21] Bruce, M. I.; Liddell, M. J.; Snow, M. R.; Tiekink, E. R. T. *Organometallics* **1988**, *7*, 343–350.

indicated. NaOMe was used as an aid to ionization.[22] Solutions were injected into a Varian Platform II spectrometer via a 10 mL injection loop. Nitrogen was used as the drying and nebulizing gas. Ions listed are the most intense in the isotope envelopes. Elemental analyses were by CMAS, Belmont, Vic., Australia.

Reagents. The compounds $(MeS)_2C=C(CN)_2$ (**2**),[23] *trans*-$(NC)(MeO_2C)C=C(CN)(CO_2Me)$ (**3**),[24] $Ru(C\equiv CR)(PPh_3)_2Cp$ (R = Ph **4a**,[25] Fc **4b**,[2j] $C\equiv CPh$ **10**[2g]), and $Ru(C\equiv CPh)(CO)(PPh_3)Cp$ (**7**)[16,26] were synthesized by the cited literature procedures.

Reactions of $Ru(C\equiv CPh)(PPh_3)_2Cp$ with $(MeS)_2C=C(CN)_2$. (a) Complex **4a** (0.50 g, 0.63 mmol) and **2** (0.13 g, 0.78 mmol) were added to benzene (25 mL), and the mixture was heated at reflux point under N_2 for 24 h. The initially yellow solution gradually became deep claret in color. After cooling, the solution was concentrated under reduced pressure, and the residue was separated on a column of basic alumina. Elution with CH_2Cl_2 gave a yellow band, which contained a mixture of starting materials (0.43 g); further elution with acetone/CH_2Cl_2 (1:9) gave a maroon band, which was further purified by recrystallization (CH_2Cl_2/MeOH) to afford $Ru\{C_5Ph(SMe)(CN)=N(SMe)\}(PPh_3)Cp$ (**5a**) as dark red blocks (115 mg, 26%). Crystals for X-ray analysis were grown by slow evaporation of a CH_2Cl_2 solution layered with MeOH. Anal. Calcd ($C_{37}H_{31}N_2PRuS_2$): C, 63.50; H, 4.46; N, 4.00; *M*, 700. Found: C, 63.59; H, 4.41; N, 3.90. IR (Nujol, cm^{-1}): ν_{max} 3054w, 2192vs, 1463vs, 1432m, 1346m, 1289s, 1106m, 1090m, 695s. ^1H NMR: δ 7.29−7.46 (20H, m), 4.74 (5H, s), 2.67 (3H, br s), 1.65 (3H, s). ^{13}C NMR: δ 126.8−138.8 (m), 84.6 [d, *J*(CP) = 1.9 Hz), 82.6 [d, *J*(CP) = 2.0 Hz], 60.3, 26.1. ^{31}P NMR: δ 51.5. ES-MS (*m/z*): 723, $[M + Na]^+$; 718, $[M + NH_4]^+$; 700, M^+.

(b) Complex **4a** (200 mg, 0.25 mmol), **2** (53 mg, 0.31 mmol), and AIBN (20 mg) were added to benzene (10 mL), and the mixture was heated to reflux under N_2 for 24 h. A second portion of AIBN (20 mg) was added after 5 h. The initially yellow solution gradually became a deep claret color. Workup and purification as above afforded **5a** (73 mg, 42%).

(c) Complex **4a** (200 mg, 0.25 mmol) and **2** (53 mg, 0.31 mmol) were added to benzene (10 mL), and the mixture was illuminated with a 300 W sun lamp under N_2 for 24 h. The initially yellow solution became a deep claret color after a few minutes and began to reflux after ca. 30 min. Workup and purification as above afforded **5a** (124 mg, 71%).

Reaction of $Ru(C\equiv CFc)(PPh_3)_2Cp$ with $(MeS)_2C=C(CN)_2$. $Ru(C\equiv CFc)(PPh_3)_2Cp$ (**4b**) (200 mg, 0.22 mmol) and **2** (47 mg, 0.28 mmol) were added to benzene (10 mL), and the mixture was heated to reflux under N_2 for 48 h. The pale yellow solution gradually acquired a deep claret color. After cooling, the solution was concentrated under reduced pressure and the residue was purified by column chromatography (basic alumina). Elution with CH_2Cl_2 gave a yellow band containing a mixture of unreacted starting materials (176 mg); further elution with 1:9 acetone/CH_2Cl_2 gave a maroon band, which was further purified by recrystallization from CH_2Cl_2/MeOH to afford $Ru\{C_5Fc(SMe)(CN)=N(SMe)\}(PPh_3)Cp$ (**5b**) as dark red prisms (50 mg, 28%). Crystals for X-ray analysis were grown by slow evaporation of a CH_2Cl_2 solution layered with MeOH. Anal. Calcd ($C_{41}H_{35}FeN_2PRuS_2$): C, 60.96; H, 4.37; N, 3.47; *M*, 808. Found: C, 59.96; H, 4.47; N, 3.35. IR (Nujol, cm^{-1}): ν_{max} 2192s, 1467s, 1433vs, 1269s, 1189m, 1133m, 1105m, 1090m, 910m, 729s, 694s. ^1H NMR: δ 7.16−7.38 (15H, m), 4.85 (5H, s), 4.66 (1H, br s), 4.44 (1H, br s), 4.27 (2H, m), 4.11 (5H, s), 2.16 (3H, br s), 1.25 (3H, s). ^{13}C NMR: δ 133.3 [d, *J*(CP) = 10.6 Hz], 132.1 [d, *J*(CP) = 10.0 Hz], 130.5, 128.3 [d, *J*(CP) = 9.7 Hz], 93.6, 85.4, 83.6, 72.2, 71.5, 69.6, 69.1, 66.3, 29.7, 26.3. ^{31}P NMR: δ 48.5. ES-MS (*m/z*): 831, $[M + Na]^+$; 808, M^+.

Reaction of $Ru(C\equiv CPh)(CO)(PPh_3)Cp$ with $(NC)_2C=C(SMe)_2$. $Ru(C\equiv CPh)(CO)(PPh_3)Cp$ (**7**) (139 mg, 0.25 mmol) and **2** (53 mg, 0.31 mmol) were added to benzene (10 mL), and the mixture was heated to reflux under N_2 for 48 h. The pale yellow solution gradually became deep claret. After cooling, the solution was concentrated under reduced pressure and the residue was purified by column chromatography (basic alumina). Elution with CH_2Cl_2 gave a yellow band containing unreacted starting materials (95 mg); further elution with 1:9 acetone/CH_2Cl_2 gave a maroon band, which was further purified by recrystallization from CH_2Cl_2/MeOH to afford $Ru\{C(SMe)=CPhC(SMe)=C(CN)_2\}(CO)(PPh_3)Cp$ (**8**) as dark red needles (56 mg, 31%). Crystals for X-ray analysis were grown by slow evaporation of a CH_2Cl_2 solution layered with MeOH. Anal. Calcd ($C_{38}H_{31}N_2OPRuS_2$): C, 62.71; H, 4.29; N, 3.85; *M*, 728. Found: C, 62.79; H, 3.90; N, 4.23. IR (Nujol, cm^{-1}): ν_{max} 3057w, 2251w, 2210s, 2098w, 1940vs, 1479s, 1434vs, 1315m, 1234m, 1091s, 1027m, 998m, 910s, 838s, 812s, 732s, 695s. ^1H NMR: δ 7.33−7.53 (20H, m), 5.18 (5H, s), 2.25 (3H, s), 1.50 (3H, s). ^{13}C NMR: δ 204.8 [d, *J*(CP) = 20.3 Hz], 189.5, 188.3, 142.9, 138.2, 135.5 [d, *J*(CP) = 48.1 Hz], 133.7 [d, *J*(CP) = 10.6 Hz], 130.1, 128.5 [d, *J*(CP) = 3.8 Hz], 128.3 [d, *J*(CP) = 10.0 Hz], 127.9, 126.0, 117.1, 114.8, 112.7, 90.5, 26.7, 17.7. ^{31}P NMR: δ 50.1. ES-MS (*m/z*): 751, $[M + Na]^+$.

Further elution with acetone/CH_2Cl_2 (1:9) gave a yellow band, which was further purified by slow recrystallization from CH_2Cl_2/MeOH to afford $Ru\{C(SMe)=CPhC(SMe)=C(CN)_2\}(PPh_3)Cp$ (**9**) as dark yellow rods and plates (13 mg, 11%), suitable for X-ray analysis. Anal. Calcd ($C_{20}H_{16}N_2ORuS_2$): C, 51.60; H, 3.46; N, 6.02; *M*, 466. Found: C, 51.47; H, 3.54; N, 6.13. IR (Nujol, cm^{-1}): ν_{max} 2200s, 1953vs, 1470vs, 1351m, 1323s, 1303s, 698s. ^1H NMR: δ 7.33−7.46 (5H, m), 5.21 (5H, s), 2.83 (3H, s), 2.51 (3H, s). ^{13}C NMR: δ 201.1, 170.5, 144.1, 137.5, 128.0−133.8 (m), 117.6, 112.5, 89.5, 86.0, 32.8, 29.7, 26.4. ES-MS (*m/z*): 489, $[M + Na]^+$.

Reaction of $Ru(C\equiv CC\equiv CPh)(PPh_3)_2Cp$ with $(MeS)_2C=C(CN)_2$. $Ru(C\equiv CC\equiv CPh)(PPh_3)_2Cp$ (**10**) (160 mg, 0.20 mmol) and **2** (41 mg, 0.24 mmol) were added to benzene (10 mL), and the mixture was heated at reflux point for 48 h. The pale yellow solution gradually became deep claret. After cooling, the solution was concentrated under reduced pressure and the residue was purified on a column of basic alumina. Elution with CH_2Cl_2 gave a mixture of yellow and purple bands (fraction A); further elution with 1:9 acetone/CH_2Cl_2 gave a mixture of purple and blue-green bands (fraction B). Fraction A was further purified by preparative TLC (silica, CH_2Cl_2) to afford $Ru\{C\equiv CC(SMe)=CPhC(SMe)=C(CN)_2\}(PPh_3)_2Cp$ (**12**) as a dark red solid (26 mg, 13%), which was found to exist in $CDCl_3$ solution as a ca. 3:2 mixture of isomers or rotamers by NMR. Anal. Calcd ($C_{57}H_{46}N_2P_2RuS_2$): C, 69.42; H, 4.70; N, 2.84; *M*, 986. Found: C, 70.89; H, 5.38; N, 1.57. IR (Nujol, cm^{-1}): ν_{max} 3053m, 2218m, 2017vs, 1497m, 1479s, 1434vs, 1089m, 741m, 695vs ^1H NMR: δ 7.02−7.42 (35H, m), 4.46 (5H, s, major), 4.33 (5H, s, minor), 2.242 (3H, s, minor), 2.237 (3H, s, major), 2.19 (3H, s, minor), 1.73 (3H, s, major). ^{13}C NMR: δ 186.6, 185.9, 124.4−138.9 (m), 114.4, 114.1, 113.6, 112.1, 96.6, 94.3, 91.0, 89.9, 86.4, 86.1, 81.4, 79.9, 29.7, 16.7, 16.1, 15.9. ^{31}P NMR: δ 47.4 (major), 47.1 (minor). ES-MS (*m/z*): 1009, $[M + Na]^+$; 987, $[M + H]^+$.

A second dark red band yielded a small amount of **11**, which was added to that obtained from fraction B (see below). Extensive decomposition of the initially yellow band was observed, characteristic of the behavior of **10** on silica.

Fraction B was further purified by preparative TLC (silica, CH_2Cl_2) to afford $Ru\{C(SMe)=C(C\equiv CPh)C(SMe)=C(CN)_2\}(PPh_3Cp$ (**11**) as a dark red solid (total yield 27 mg, 19%). Dark red

---

[22] Henderson, W.; McIndoe, J. S.; Nicholson, B. K.; Dyson, P. J. *J. Chem. Soc., Dalton Trans.* **1998**, 519.

[23] Gompper, R.; Töpfl, W. *Chem. Ber.* **1962**, *95*, 2861–2870.

[24] Ireland, C. J.; Jones, K.; Pizey, J. S. *Synth. Commun.* **1976**, *6*, 185–191.

[25] Bruce, M. I.; Hameister, C.; Swincer, A. G.; Wallis, R. C. *Inorg. Synth.* **1982**, *21*, 82.

[26] Bruce, M. I.; Wallis, R. C. *Aust. J. Chem.* **1979**, *32*, 1471–1485.

Table 2. Crystal Data and Refinement Details

	5a	**8**·CH_2Cl_2	**9**	**9′**	**11**	**13**
formula	$C_{37}H_{31}N_2PRuS_2$	$C_{38}H_{31}N_2OPRuS_2$. CH_2Cl_2	$C_{20}H_{16}N_2ORuS_2$	$C_{20}H_{16}N_2ORuS_2$	$C_{39}H_{31}N_2PRuS_2$	$C_{39}H_{31}N_2O_4PRu$
MW	699.80	812.79	465.56	465.56	723.87	723.73
cryst syst	triclinic	triclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a/Å	10.360(2)	11.0170(9)	11.2373(7)	10.481(2)	9.720(2)	14.400(1)
b/Å	11.557(1)	12.958(1)	14.7510(6)	17.294(2)	13.312(2)	10.7480(9)
c/Å	13.634(1)	13.858(1)	11.6038(5)	10.778(1)	13.636(3)	22.054(2)
α/deg	88.422(8)	113.835(1)			97.32(2)	
β/deg	80.42(1)	91.729(2)	95.161(4)	103.730(4)	100.57(2)	103.395(2)
γ/deg	78.75(1)	96.604(1)			108.64(2)	
V/Å^3	1579	1791	1916	1898	1610	3320
ρ_c/g cm^{-3}	1.47_2	1.50_7	1.61_4	1.62_9	1.49_3	1.44_8
Z	2	2	4	4	2	4
$2\theta_{max}$/deg	70	66	74	67	50	75
μ(Mo Kα)/mm^{-1}	0.71	0.78	1.047	1.057	0.70	0.57
$T_{min/max}$	0.89	0.88	0.82	0.75	0.86	0.87
cryst dimens/mm^3	0.31 × 0.23 × 0.10	0.48 × 0.21 × 0.18	0.46 × 0.35 × 0.10	0.43 × 0.15 × 0.12	0.28 × 0.13 × 0.015	0.42 × 0.36 × 0.14
N_{tot}	71 485	26 771	90 519	31 882	10 883	65 402
N (R_{int})	13 639 (0.032)	12 879 (0.015)	9440 (0.023)	7136 (0.032)	5525 (0.050)	17 252 (0.050)
N_o	9943	11480	7877	6231	2550	11506
R [$I > 2\sigma(I)$]	0.032	0.031	0.047	0.027	0.061	0.051
R_w [$I > 2\sigma(I)$] (n_w)	0.088 (–)	0.066 (4)	0.095 (8)	0.056 (5)	0.135 (40)	0.102 (20)
S	1.04	1.00	1.06	0.93	0.90	0.98
$\|\Delta\rho_{max}\|$/e Å^{-3}	1.68	1.12	2.14	0.84	3.4	4.0
T/K	100	150	100	150	100	170

needles suitable for X-ray analysis were grown by slow evaporation of a CH_2Cl_2 solution layered with MeOH. Anal. Calcd ($C_{39}H_{31}N_2PRuS_2$): C, 64.71; H, 4.32; N, 3.87; *M*, 724. Found: C, 65.13; H, 4.41; N, 3.88. IR (Nujol, cm^{-1}): ν_{max} 3055w, 2195vs, 1466vs, 1433vs, 1277vs, 1221m, 1165m, 1091s, 909m, 731vs, 694vs. ^{1}H NMR: δ 7.21−7.63 (20H, m), 4.84 (5H, s), 2.70 (3H, br s), 2.50 (3H, s). ^{13}C NMR: δ 198.2, 127.7−133.6 (m), 115.6, 102.1, 85.7, 84.8, 84.1, 29.7, 26.0. ^{31}P NMR: δ 50.4. ES-MS (*m*/*z*): 747, [M + Na]$^+$; 719, [Ru(CO)(PPh$_3$)$_2$Cp]$^+$.

Reaction of Ru(C≡CPh)(PPh$_3$)$_2$Cp with Dimethyl 2,3-Dicyanofumarate. Complex **4a** (0.50 g, 0.63 mmol) and **3** (0.15 g, 0.78 mmol) were added to benzene (25 mL), and the mixture was heated at reflux point for 2 h. The yellow-green solution became deep claret after a few minutes and eventually turned intense violet. After cooling, the solution was concentrated under reduced pressure and the residue was purified by column chromatography (basic alumina). Elution with CH_2Cl_2 gave a yellow band (49 mg), which contained recovered **4a**; further elution with 1:9 EtOAc/CH_2Cl_2 afforded a yellow-orange band, which was further purified by preparative TLC (silica, 1:49 acetone/CH_2Cl_2) to afford Ru{C[═C(CN)$_2$]-CPh═C(CN)(CO$_2$Me)}(PPh$_3$)Cp (**13**) as an orange microcrystalline solid (88 mg, 21% based on recovered starting material) as an approximately 3:2 mixture of isomers. Crystals for X-ray analysis were grown by slow evaporation of a CH_2Cl_2 solution layered with MeOH. Anal. Calcd ($C_{39}H_{31}N_2O_4PRu$): C, 64.63; H, 4.31; N, 3.87; *M*, 722. Found: C, 64.70; H, 4.27; N, 3.89. IR (Nujol, cm^{-1}): ν_{max} 3058m, 2250w, 2212s, 1974m, 1916m, 1715vs, 1615s, 1482m, 1434vs, 1324m, 1282s, 1237vs, 1190m, 1122m, 1090s, 912m, 729s, 697vs. ^{1}H NMR: δ 7.32−7.50 (20H, m), 4.69 (5H, s, minor), 4.61 (5H, s, major), 3.77 (3H, s, minor), 3.44 (3H, s, major), 3.39 (3H, s, minor), 2.63 (3H, s, major). ^{13}C NMR: δ 170.2, 170.1, 159.1, 159.0, 127.8−137.7 (m), 122.1, 119.4, 105.7, 91.2, 90.4, 69.8, 52.2, 51.9, 51.7. ^{31}P NMR: δ 44.6 (minor), 37.3 (major). ES-MS (*m*/*z*): 748, [M + Na]$^+$; 723, [M + H]$^+$.

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. All data were measured using monochromatic Mo Kα radiation, $\lambda = 0.71073$ Å. Anisotropic displacement parameter forms were refined for the non-hydrogen atoms, (x, y, z, $U_{iso})_H$ being included following a riding model. Conventional residuals R, R_w on $|F^2|$ are quoted [weights: $(\sigma_2(F^2) + 0.00nwF^2)^{-1}$]. Neutral atom complex scattering factors were used; computation used the XTAL 3.7 program system.[27] Pertinent results are given in the figures (which show non-hydrogen atoms with 50% probability amplitude displacement ellipsoids and hydrogen atoms with arbitrary radii of 0.1 Å) and in Tables 1 and 2.

Variata. 5a. Refinement was executed using the SHELXL-97 program;[28] reflection weights were $[\sigma_2(F^2) + (0.50P)^2]^{-1}$ [$P = (F_o^2 + 2F_c^2)/3$]. Residuals cited are R1 and wR2.

9. As presented, the sample comprised crystals with two different morphologies, both determined and found to be polymorphs, both monoclinic $P2_1/c$, the "plate" form denoted **9** and the "rod" form as **9′**.

Final atomic positional coordinates, with estimated standard deviations, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre under deposition numbers 655563−655568.

Acknowledgment. We thank Professor Brian Nicholson (University of Waikato, Hamilton, New Zealand) for providing the mass spectra, Dr. Simon Pyke for helpful discussions on NMR, the ARC for support of this work, and Johnson Matthey plc, Reading, for a generous loan of RuCl$_3$·nH$_2$O.

Supporting Information Available: CIF files for the X-ray structures. This material is available free of charge via the Internet at http://pubs.acs.org.

OM7011437

---

(27) Hall, S. R., du Boulay, D. J., Olthof-Hazekamp, R., Eds. *The XTAL 3.7 System*; University of Western: Australia, 2000.

(28) Sheldrick, G. M. *SHELXL-97, A Program for Crystal Structure Refinement*; University of Göttingen, 1997.