

# A New Carbon-Hydrogen Bond Activation Reaction: Stereospecific Abstraction of Vinyllic Protons from Rhenium Alkene Complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H}_2\text{C}=\text{CHR})]^+\text{BF}_4^-$ by the Base $t\text{-BuO}^-\text{K}^+$

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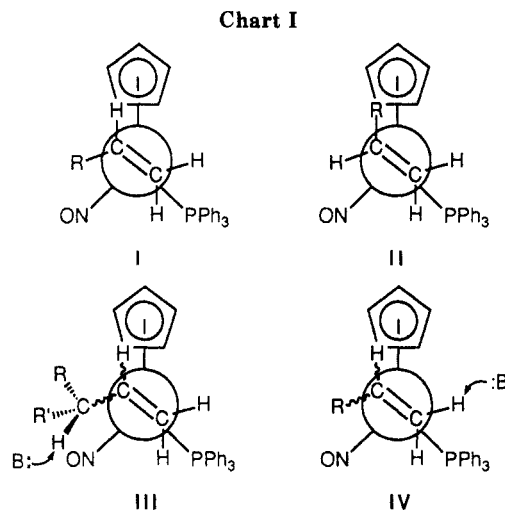
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**Summary:** The title reaction gives the vinyl complexes  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}=\text{CHR})$  for  $\text{R} = \text{CH}(\text{CH}_3)_2$  and  $\text{C}_6\text{H}_5$ ; deuterium labeling and NMR experiments show that only one of the two geminal alkene ligand protons is abstracted.

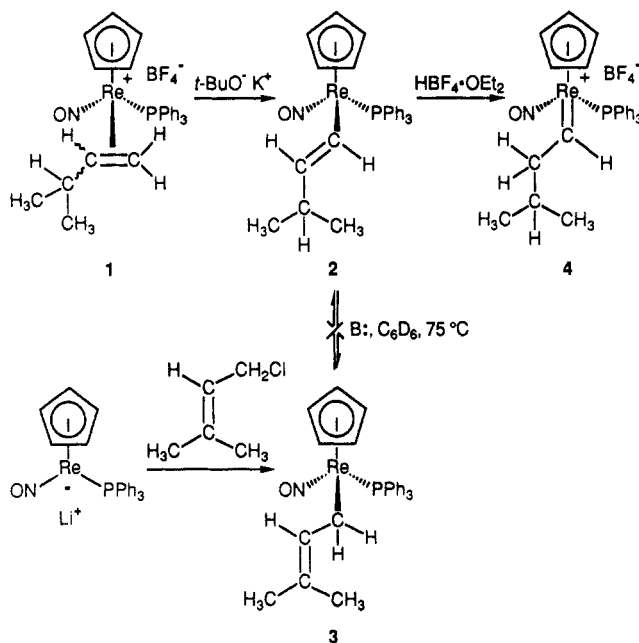
Many cationic alkene complexes  $[\text{L}_n\text{M}(\text{H}_2\text{C}=\text{C}(\text{R}')\text{-CH}_2\text{R})]^+$  undergo allylic deprotonation by amine and alkoxide bases.<sup>1,2</sup> Neutral  $\sigma$ -allyl complexes  $\text{L}_n\text{M}(\text{CH}_2\text{C}(\text{R}')=\text{CHR})$  are subsequently isolated in high yields. This transformation is widely presumed to have considerable generality. Accordingly, we recently found that the rhenium alkene complexes  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H}_2\text{C}=\text{C}(\text{R}')\text{CH}_2\text{R})]^+\text{X}^-$  ( $\text{R}/\text{R}' = \text{H}/\text{H}$ ,  $\text{C}_6\text{H}_5/\text{H}$ ,  $\text{H}/\text{CH}_3$ ) and  $t\text{-BuO}^-\text{K}^+/t\text{-BuOH}$  react to give the  $\sigma$ -allyl complexes  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_2\text{C}(\text{R}')=\text{CHR})$ .<sup>2</sup> We sought to extend this simple reaction to a wider number of substrates. In this communication, we describe a facile, apparently unprecedented, and stereospecific alternative vinyllic deprotonation mode that provides a new alkene carbon-hydrogen bond activation protocol.

The 3-methyl-1-butene complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H}_2\text{C}=\text{CHCH}(\text{CH}_3)_2)]^+\text{BF}_4^-$  (**1**)<sup>3</sup> was prepared as a (67 ± 2):(33 ± 2) mixture of *RS,SR/RR,SS* diastereomers by methods described previously.<sup>4</sup> The diastereomers differ in the alkene enantioface bound to rhenium, exhibit idealized structures I and II (Chart I), and do not interconvert at room temperature. A THF suspension of **1** was treated with  $t\text{-BuO}^-\text{K}^+/t\text{-BuOH}$  (0.5 M; Scheme I). Workup gave a neutral product (**2**, 84%), which was characterized by NMR and IR spectroscopy.<sup>5</sup> Surprisingly, the data more closely matched that expected for a vinyl,<sup>6</sup> as opposed to an allyl,<sup>2</sup> complex. Hence, a <sup>13</sup>C NMR spectrum was recorded without proton decoupling. Both olefinic carbons gave doublets (<sup>1</sup>*J*<sub>C(α)H</sub>/<sup>1</sup>*J*<sub>C(β)H</sub> = 134/147 Hz) indicative of one directly bound hydrogen. Thus, **2** was assigned the structure  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}=\text{CHCH}(\text{CH}_3)_2)$ .

An authentic sample of the alternative deprotonation product, the allyl complex  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)$ -



Scheme I. Vinyllic Deprotonation of the 3-Methyl-1-butene Complex **1**



$(\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2)$  (**3**), was sought. Thus, the "anion"<sup>7</sup>  $\text{Li}^+[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)]^-$  was treated with the allylic chloride  $\text{ClCH}_2\text{CH}=\text{C}(\text{CH}_3)_2$  (Scheme I). Workup gave **3** in 97% yield.<sup>8</sup> We sought to determine which deprotonation product was more stable, **2** or **3**. However, both remained unchanged when treated with  $(\text{C}_2\text{H}_5)_3\text{N}$  or  $t\text{-BuO}^-\text{K}^+/t\text{-BuOH}$  in  $\text{C}_6\text{D}_6$  (75 °C, 8 h).

The alkylidene complexes  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(=\text{CHCH}_2\text{R})]^+\text{X}^-$  also react with mild bases to give the vinyl

(1) (a) Rosenblum, M. J. *Organomet. Chem.* **1986**, *300*, 191. (b) Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancredi, J.; Wells, D. J. *Am. Chem. Soc.* **1976**, *98*, 3495.

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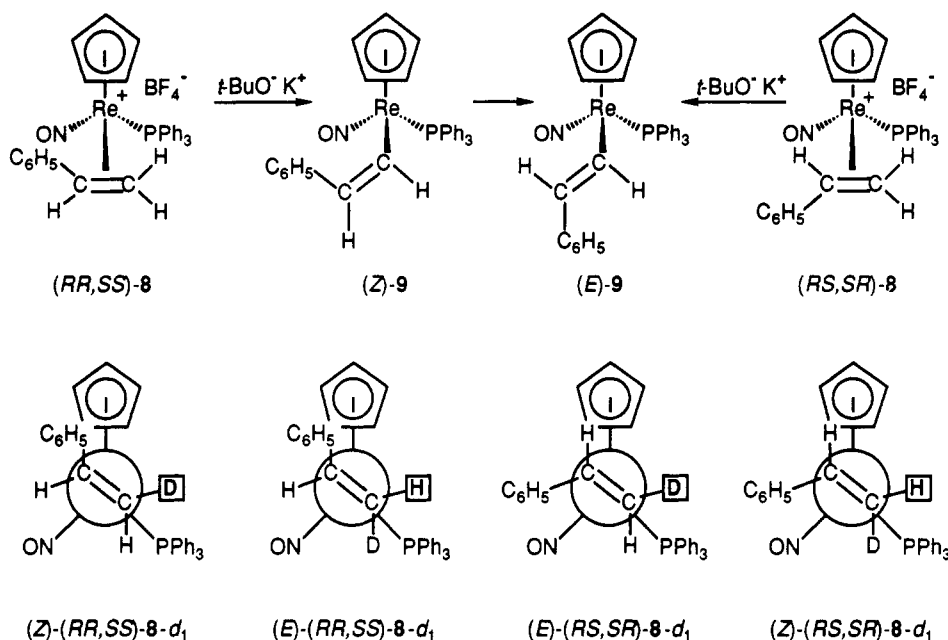
(3) Complex **1** was characterized by IR and NMR spectroscopy and microanalysis. Its properties were similar to those of alkene complexes reported earlier.<sup>4</sup>

(4) Bodner, G. S.; Peng, T.-S.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1191. *R/S* nomenclature conventions are described in this paper.

(5) Complex **2** is isolated as a (97 ± 2):(3 ± 2) mixture of *E/Z* C=C isomers (95 ± 2):(5 ± 2) after 2 days in  $\text{C}_6\text{D}_6$ .<sup>6b</sup> Selected data for (*E*)-**2**: <sup>1</sup>H NMR ( $\delta$ ,  $\text{C}_6\text{D}_6$ ) 7.96 (ddd, *J* = 16.5, 2.9, 1.1 Hz, *H}\_\alpha*), 5.38 (ddd, *J* = 16.5, 6.4, 2.2 Hz, *H}\_\beta*), 4.67 (s,  $\text{C}_5\text{H}_5$ ), 2.50 (m, *H}\_\gamma*), 1.03 (d, *J* = 6.6 Hz,  $\text{CH}_3$ ), 0.99 (d, *J* = 6.6 Hz,  $\text{CH}_3$ ); <sup>13</sup>C NMR (ppm,  $\text{C}_6\text{D}_6$ ) 145.3 (br s,  $\text{C}_\alpha$ ), 119.7 (d, *J*<sub>CP</sub> = 11.8 Hz,  $\text{C}_\alpha$ ), 38.0 (s,  $\text{C}_\gamma$ ), 24.2 (s,  $\text{C}_\beta$ ), 24.1 (s,  $\text{C}_\gamma$ ); <sup>31</sup>P NMR (ppm,  $\text{C}_6\text{D}_6$ ) 22.0 (s); IR (cm<sup>-1</sup>, thin film)  $\nu_{\text{NO}}$  1635 s. Anal. Calcd for  $\text{C}_{28}\text{H}_{29}\text{NOPRe}$ : C, 54.89; H, 4.77; N, 2.29. Found: C, 55.14; H, 4.86; N, 2.40.

(6) (a) Bodner, G. S.; Smith, D. E.; Hatton, W. G.; Heah, P. C.; Georgiou, S.; Rheingold, A. L.; Geib, S. J.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7688. (b) Criteria for distinguishing *E/Z* C=C isomers of vinyl complexes are described in this paper.

(7) Crocco, G. L.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 6110. (8) Selected data for **3**: <sup>1</sup>H NMR ( $\delta$ ,  $\text{C}_6\text{D}_6$ ) 6.01 (ddd, *J* = 8.9, 8.9, 0.8 Hz, *H}\_\alpha*), 4.64 (s,  $\text{C}_5\text{H}_5$ ), 3.18 (m, *H}\_\gamma*), 2.65 (ddd, *J* = 8.9, 8.9, 2.8 Hz, *H}\_\beta*), 1.98 (s,  $\text{CH}_3$ ), 1.90 (s,  $\text{CH}_3$ ); <sup>13</sup>C NMR (ppm,  $\text{C}_6\text{D}_6$ ) 139.6 (d, *J*<sub>CP</sub> = 3.9 Hz,  $\text{C}_\alpha$ ), 120.3 (s,  $\text{C}_\gamma$ ), 26.4 (s,  $\text{C}_\beta$ ), 18.0 (s,  $\text{C}_\gamma$ ), -11.3 (d, *J*<sub>CP</sub> = 4.9 Hz,  $\text{C}_\alpha$ ); <sup>31</sup>P NMR (ppm,  $\text{C}_6\text{D}_6$ ) 26.1 (s); IR (cm<sup>-1</sup>, thin film)  $\nu_{\text{NO}}$  1627 s. Anal. Calcd for  $\text{C}_{28}\text{H}_{29}\text{NOPRe}$ : C, 54.89; H, 4.77; N, 2.29. Found: C, 55.15; H, 4.87; N, 2.30.

Scheme II. Deprotonation of Styrene Complexes 8<sup>a</sup>

<sup>a</sup> Protons or deuterium atoms abstracted by base are shown in boldface.

complexes  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}=\text{CHR})$ .<sup>6</sup> We therefore considered the possibility that the alkene complex 1 might be in rapid equilibrium with a small amount of the alkylidene  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(=\text{CHCH}_2\text{CH}(\text{CH}_3)_2)]^+\text{BF}_4^-$  (4; Scheme I), which would then be the reactive species toward base. Thus, 2 was treated with  $\text{HBF}_4 \cdot \text{OEt}_2$  ( $\text{CH}_2\text{Cl}_2$ ,  $-78^\circ\text{C}$ ). Workup gave 4 in 95% yield.<sup>9</sup> The independent stability of 1 and 4 with respect to one another at room temperature precludes any pre-equilibrium isomerization prior to deprotonation.

Allylic deprotonations of cationic alkene complexes are commonly viewed as proceeding via transition states with the carbon-hydrogen bond antiperiplanar to the  $\text{C}-\text{C}-\text{M}$  moiety, as sketched in III (Chart I).<sup>1</sup> In 1, this would force the geminal methyl groups toward the rhenium ligands. This might sterically disfavor allylic deprotonation relative to other processes. We therefore conducted an analogous reaction of the 1-pentene complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H}_2\text{C}=\text{CHCH}_2\text{CH}_2\text{CH}_3)]^+\text{BF}_4^-$  (5;  $96 \pm 2$ ): $(4 \pm 2)$  *RS,SR/RR,SS*), which would direct only an ethyl group toward the rhenium ligands in III. <sup>1</sup>H NMR analysis indicated a ca. 84:16 mixture of the known vinylic deprotonation product  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}=\text{CHCH}_2\text{CH}_2\text{CH}_3)$  (6)<sup>8</sup> and the allylic deprotonation product  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_3)$  (7).<sup>10</sup> Other substrates bearing a single allylic substituent give much greater amounts of allyl complexes.<sup>2,11</sup> However, the exact base employed (cf. *t*-BuO<sup>-</sup>K<sup>+</sup>/*t*-BuOH vs *t*-BuO<sup>-</sup>K<sup>+</sup>/THF) also exhibits a major influence.<sup>11</sup>

Next, alkene complexes lacking allylic protons were studied. The diastereomeric styrene complexes (*RS,SR*)- and (*RR,SS*)- $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H}_2\text{C}=\text{CHC}_6\text{H}_5)]^+\text{BF}_4^-$  (*(RS,SR)-8*, (*RR,SS)-8*)<sup>4</sup> were separately treated with

*t*-BuO<sup>-</sup>K<sup>+</sup>/THF (Scheme II). Styryl complex (*E*)- $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}=\text{CHC}_6\text{H}_5)$  (*(E)-9*)<sup>12</sup> was subsequently isolated in 90–91% yields. Both reactions were repeated and worked up at  $-25^\circ\text{C}$ , and the crude products were dissolved in  $\text{CD}_2\text{Cl}_2$  at  $-78^\circ\text{C}$ . <sup>1</sup>H NMR analysis clearly showed the kinetic product from (*RS,SR*)-8 to be (*E*)-9 and that from (*RR,SS*)-8 to be the C=C geometric isomer (*Z*)-9 ( $(97 \pm 2)$ ): $(3 \pm 2)$  *Z/E*). Complex (*Z*)-9 isomerized, at erratic rates, to (*E*)-9 at room temperature ( $\geq 99:1$  *E/Z*).

The preceding data strongly suggested that vinylic deprotonation was stereospecific. Thus, the monodeuterated styrene complexes 8-*d*<sub>1</sub> in Scheme II were prepared by methods described previously.<sup>4,13</sup> All underwent, within the limits of detection, stereospecific deprotonation as shown. The results establish that (a) the deprotonation site is determined by the configuration at rhenium, as opposed to that of the =CHR terminus, and (b) the rhenium occupies the position of the abstracted proton in the product.

On the basis of the above data, IV (Chart I) constitutes a reasonable transition-state model for vinylic deprotonation. However, it should be emphasized that concerted and stepwise variants are possible, and that other Re-(C=C) rotamers might also be reactive. The stereospecificity suggests a parallel to electrocyclic ring openings of aziridines and cyclopropyl anions.<sup>14</sup>

We do not presently have a rationale for the ease of these transformations. The vinylic protons of the cationic rhenium-bound alkenes clearly exhibit much greater kinetic and thermodynamic acidities than those of free al-

(9) Complex 4 forms as a  $(98 \pm 2)$ : $(2 \pm 2)$  mixture of *ac/sc* isomers at  $-78^\circ\text{C}$  and equilibrates to a  $(95 \pm 2)$ : $(5 \pm 2)$  mixture at room temperature. Selected data for *ac-4*: <sup>1</sup>H NMR ( $\delta$ ,  $\text{CD}_2\text{Cl}_2$ ) 15.81 (dd,  $J = 9.3, 5.4$  Hz,  $\text{H}_\alpha$ ), 5.98 (s,  $\text{C}_6\text{H}_5$ ), 3.26 (ddd,  $J = 15.6, 9.3, 6.5$  Hz,  $\text{H}_\beta$ ), 1.97 (ddd,  $J = 15.6, 5.4, 5.4$  Hz,  $\text{H}_\gamma$ ); <sup>13</sup>C NMR (ppm,  $\text{CD}_2\text{Cl}_2$ ) 313.3 (d,  $J_{\text{CP}} = 7.3$  Hz,  $\text{C}_\alpha$ ), 99.6 (s,  $\text{C}_5\text{H}_5$ ), 66.1 (s,  $\text{C}_\beta$ ); <sup>31</sup>P NMR (ppm,  $\text{CD}_2\text{Cl}_2$ ) 18.4; IR ( $\text{cm}^{-1}$ , thin film) 1711 s. Anal. Calcd for  $\text{C}_{22}\text{H}_{30}\text{BF}_4\text{NOPrRe}$ : C, 48.01; H, 4.32; N, 2.00. Found: C, 48.11; H, 4.34; N, 1.96.

(10) Partial <sup>1</sup>H NMR data ( $\delta$ ,  $\text{C}_6\text{H}_6$ ): 6, 4.687, 4.693 (*E/Z*  $\text{C}_5\text{H}_5$ , ca. 97:3);<sup>8</sup> 7, 4.62 ( $\text{C}_5\text{H}_5$ ).

(11) These data will be detailed in our full paper.

(12) Selected data for (*E*)-9: <sup>1</sup>H NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 9.14 (dd,  $J = 17.2, 2.8$  Hz,  $\text{H}_\alpha$ ), 6.00 (dd,  $J = 17.2, 2.1$  Hz,  $\text{H}_\beta$ ), 5.14 (s,  $\text{C}_6\text{H}_5$ ); <sup>13</sup>C NMR (ppm,  $\text{CDCl}_3$ ) 136.4 (d,  $J_{\text{CP}} = 2.4$  Hz,  $\text{C}_\beta$ ), 135.5 (d,  $J_{\text{CP}} = 12.0$  Hz,  $\text{C}_\alpha$ ); <sup>31</sup>P NMR (ppm,  $\text{CDCl}_3$ ) 21.4 (s); IR ( $\text{cm}^{-1}$ , thin film) 1643 s. Anal. Calcd for  $\text{C}_{31}\text{H}_{27}\text{NOPrRe}$ : C, 57.57; H, 4.21; N, 2.17. Found: C, 57.39; H, 4.25; N, 2.18. Selected data for (*Z*)-9: <sup>1</sup>H NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 8.31 (dd,  $J = 12.8, 7.6$  Hz,  $\text{H}_\alpha$ ), 6.78 (dd,  $J = 7.6, 0.9$  Hz,  $\text{H}_\beta$ ), 5.04 (s,  $\text{C}_6\text{H}_5$ ); <sup>13</sup>C NMR (ppm,  $\text{CD}_2\text{Cl}_2$ ) 137.1 (s,  $\text{C}_\beta$ ), 131.9 (d,  $J_{\text{CP}} = 10.6$  Hz,  $\text{C}_\alpha$ ).

(13) Peng, T.-S.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* 1990, 902.

(14) Boche, G.; Walborsky, H. M. In *The Chemistry of The Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: New York, 1987; Part 1, pp 788–794.

kenes.<sup>15</sup> Interestingly, basic sites or additives are frequently found in the heterogeneous metal-based catalysts used to process coal- and petroleum-derived feedstocks.<sup>16</sup> Thus, analogous acid/base chemistry of intermediate catalyst/alkene complexes may occur. Additional examples of vinylic deprotonations of alkene complexes will be

reported in the near future.<sup>17</sup>

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(15) Brandsma, L.; Verkruijse, H. D.; Schade, C.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* 1986, 260.

(16) E.g.: Lamb, H. H.; Gates, B. C. *J. Am. Chem. Soc.* 1986, 108, 81.

(17) Kowalczyk, J. J.; Arif, A. M.; Gladysz, J. A. Submitted for publication.

## Articles

### Cyclopentadienylruthenium and -osmium Chemistry. 33.<sup>1</sup> Cyclobutenyl-Nitrile Complexes. X-ray Structures of $\text{Ru}[\text{C}=\text{CPhC}(\text{CF}_3)_2\text{C}(\text{CN})_2](\text{NCMe})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$ and $[\text{Ru}[\text{C}=\text{CPhC}(\text{CF}_3)_2\text{C}(\text{CN})_2](\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]_2\text{-}$ $[\mu\text{-(NC)}_2\text{C}=\text{C}(\text{CF}_3)_2]$

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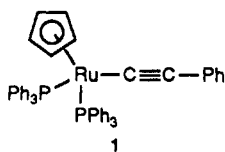
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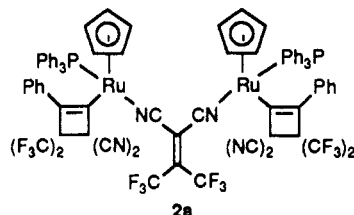
Replacement of MeCN in  $\text{Ru}[\text{C}=\text{CPhC}(\text{CF}_3)_2\text{C}(\text{CN})_2](\text{NCMe})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$ , readily obtained from the bis- $\text{PPh}_3$  complex in MeCN, by a series of organonitrile ligands ( $\text{CH}_2=\text{CHCN}$ , *trans*- $\text{CH}(\text{CH})=\text{CH}(\text{CN})$ ,  $\text{C}(\text{CN})_2=\text{C}(\text{CF}_3)_2$  (dcfe),  $\text{C}_2(\text{CN})_4$ , *o*- $\text{C}_6\text{H}_4(\text{CN})_2$ , *p*- $\text{C}_6\text{H}_4(\text{CN})_2$ , *o*- $\text{C}_6\text{F}_4(\text{CN})_2$ , *p*- $\text{C}_6\text{F}_4(\text{CN})_2$ ,  $\text{C}_6\text{H}_2(\text{CN})_4$ ) has given highly colored complexes containing one or two  $\text{Ru}[\text{C}=\text{CPhC}(\text{CF}_3)_2\text{C}(\text{CN})_2](\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$  moieties. The binuclear complexes are bridged by the di- or tetranitriles; isomers were found for the fumaronitrile, dcfe, and  $\text{C}_2(\text{CN})_4$  derivatives. The deep blue  $\mu$ -dcfe complexes are readily oxidized to green paramagnetic species that appear to contain an epoxy radical ligand. The complexes were characterized by spectroscopic and electrochemical studies and, in the case of the title complexes, by single-crystal X-ray diffraction studies. Crystals of  $\text{Ru}[\text{C}=\text{CPhC}(\text{CF}_3)_2\text{C}(\text{CN})_2](\text{NCMe})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$  (4) crystallize in the triclinic space group  $P\bar{1}$  with unit cell dimensions  $a = 13.682$  (2) Å,  $b = 15.616$  (2) Å,  $c = 9.776$  (4) Å,  $\alpha = 97.97$  (4)°,  $\beta = 92.90$  (3)°, and  $\gamma = 80.53$  (2)° with  $Z = 2$ . Crystals of  $[\text{Ru}[\text{C}=\text{CPhC}(\text{CF}_3)_2\text{C}(\text{CN})_2](\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]_2[\mu\text{-(NC)}_2\text{C}=\text{C}(\text{CF}_3)_2]$  (2a) are monoclinic, space group  $P2_1/c$ , with unit cell parameters  $a = 20.48$  (1) Å,  $b = 19.378$  (4) Å,  $c = 20.914$  (3) Å,  $\beta = 112.6$  (3)°, and  $Z = 4$ . The structures were refined by a full-matrix (blocked-matrix for 2a) least-squares procedure to final  $R = 0.059$  and  $R_w = 0.064$  for 3883 reflections with  $I \geq 2.5\sigma(I)$  for 4 and  $R = 0.045$  and  $R_w = 0.045$  for 1708 reflections for 2a.

#### Introduction

We have recently described some cycloaddition reactions of 1,1-dicyano-2,2-bis(trifluoromethyl)ethene,  $(\text{CF}_3)_2\text{C}=\text{C}(\text{CN})_2$  (dcfe), with transition-metal  $\sigma$ -acetylide complexes to give a series of cyclobutenyl, butadienyl, and allyl compounds.<sup>2</sup> En passant, we reported the reaction between dcfe and  $\text{Ru}(\text{C}_2\text{Ph})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$  (1), which af-



forded a deep blue binuclear complex that showed a weak paramagnetism (a broad ESR signal arising from ca. 0.04 unpaired electron per molecule). The complex was characterized by a single-crystal X-ray study, which revealed the binuclear structure 2, only consistent with a diamag-



(1) Part 32: Bruce, M. I.; Cifuentes, M. P.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* 1989, 359, 379.

(2) Bruce, M. I.; Hambley, T. W.; Liddell, M. J.; Snow, M. R.; Swincer, A. G.; Tiekink, E. R. T. *Organometallics* 1990, 9, 96.

netic electronic structure. In the course of resolving this problem, we have made and characterized several related complexes containing a variety of organonitriles. This