

## Propargyl complexes of ruthenium

Chris E. Shuchart, Richard R. Willis and Andrew Wojcicki \*

*Department of Chemistry, The Ohio State University, Columbus, OH 43210 (USA)*

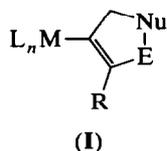
(Received May 30, 1991; in revised form July 25, 1991)

### Abstract

The first ruthenium-propargyl complexes  $\text{CpL}_2\text{RuCH}_2\text{C}\equiv\text{CPh}$  ( $\text{L} = \text{CO}$  (**1**) and  $\text{PPh}_3$  (**2**)) were synthesized by reaction of  $[\text{Cp}(\text{CO})_2\text{Ru}]^-$  with  $\text{PhC}\equiv\text{CCH}_2\text{Cl}$  or  $\text{PhC}\equiv\text{CCH}_2\text{OS}(\text{O})_2\text{C}_6\text{H}_4\text{Me-}p$  and of  $\text{Cp}(\text{PPh}_3)_2\text{RuCl}$  with  $\text{PhC}\equiv\text{CCH}_2\text{MgCl}$ , respectively. In contrast, treatment of  $[\text{Cp}(\text{CO})_2\text{Ru}]^-$  with  $\text{HC}\equiv\text{CCH}_2\text{Cl}$  affords the ruthenium- $\eta^1$ -allenyl complex  $\text{Cp}(\text{CO})_2\text{RuCH}=\text{C}=\text{CH}_2$  (**3**). Complex **1** is protonated by  $\text{HBF}_4 \cdot \text{OEt}_2$  to  $[\text{syn-Cp}(\text{CO})_2\text{Ru}(\eta^2\text{-CH}_2=\text{C}=\text{CHPh})]\text{BF}_4$  (**4a**), which isomerizes within 2 h in acetone solution at room temperature to  $[\text{anti-Cp}(\text{CO})_2\text{Ru}(\eta^2\text{-CH}_2=\text{C}=\text{CHPh})]\text{BF}_4$  (**4b**). Compound **4b** reacts with  $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$  to give the ruthenium-substituted platinum(II)- $\eta^3$ -allyl complex  $[(\eta^3\text{-CH}_2\text{C}(\text{Ru}(\text{CO})_2\text{Cp})\text{CHPh})\text{Pt}(\text{PPh}_3)_2]\text{BF}_4$  as the anti isomer quantitatively. Compound **1** undergoes facile [3+2] cycloaddition reactions with tetracyanoethylene (TCNE) and *p*-toluenesulfonyl isocyanate (TSI); the latter reaction in  $\text{CH}_2\text{Cl}_2$  solution at 25°C proceeds slightly more rapidly (1.3 times) than the corresponding reaction of  $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{C}\equiv\text{CPh}$ . With  $\text{Co}_2(\text{CO})_8$ , **1** yields the trinuclear  $(\text{CO})_3\text{Co}(\mu\text{-}\eta^2\text{-PhC}\equiv\text{CCH}_2\text{Ru}(\text{CO})_2\text{Cp})\text{Co}(\text{CO})_3$ , which undergoes very slow cleavage of the Ru- $\text{CH}_2$  bond with  $\text{CF}_3\text{CO}_2\text{H}$ , and replacement of CO (at Co) with  $\text{PPh}_3$ . The foregoing reactions are compared and contrasted with the corresponding reactions of  $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{C}\equiv\text{CPh}$ . Where a comparison has been made, **2** was found to react faster than **1**; however, its chemistry tends to be complicated by the lower stability of products and a facile  $\text{PPh}_3$ -CO ligand exchange. With TSI and  $\text{Co}_2(\text{CO})_8$ , the products are analogous to those of **1**, but with  $\text{Fe}_2(\text{CO})_9$ ,  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{RuCH}_2\text{C}\equiv\text{CPh}$  and  $\text{Fe}(\text{CO})_4\text{PPh}_3$  are obtained instead of heteronuclear metal complexes.

### Introduction

A variety of transition-metal propargyl complexes,  $\text{L}_n\text{MCH}_2\text{C}\equiv\text{CR}$ , have been prepared and their chemistry examined [1]. Earlier investigations of the chemistry focused on the reactions with protic acids to afford the metal-allene cations  $[\text{L}_n\text{M}(\eta^2\text{-CH}_2=\text{C}=\text{CHR})]^+$  and with uncharged electrophiles  $\text{E} = \text{Nu}$  to yield [3+2] cycloaddition products, **I** ( $\text{E} = \text{electrophilic part}$ ,  $\text{Nu} = \text{nucleophilic part}$ ) [2,3]. Recently, it has been shown that these complexes are useful reagents in the



synthesis of heteronuclear metal compounds, including clusters [4–8]. While one of the most-studied metal-propargyl complexes has been that of iron,  $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{C}\equiv\text{CPh}$  [1–3], the congeneric ruthenium propargyl had, until now, been unknown. Such a complex is of interest, since ruthenium compounds generally are more stable than their iron counterparts, and ruthenium tends to form clusters more readily than does iron [9,10]. Moreover, many ruthenium-containing compounds are catalytically active [11].

In this paper we report the preparation of the ruthenium propargyls  $\text{CpL}_2\text{RuCH}_2\text{C}\equiv\text{CPh}$  ( $\text{L} = \text{CO}$  (**1**) and  $\text{PPh}_3$  (**2**)) and investigations of their chemistry, with a particular focus on a comparison of **1** and  $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{C}\equiv\text{CPh}$ . Also reported is the synthesis of the allenyl complex  $\text{Cp}(\text{CO})_2\text{RuCH}=\text{C}=\text{CH}_2$  (**3**), an analogue of the known  $\text{Cp}(\text{CO})_2\text{FeCH}=\text{C}=\text{CH}_2$  [12]. The preparation and some aspects of the chemistry of **1** were presented earlier in a communication [7].

## Experimental

### General procedures

All reactions and manipulations of air-sensitive compounds were conducted by use of standard Schlenk techniques [13] under an atmosphere of Ar unless otherwise noted. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. Melting points were measured in capillary tubes and are uncorrected.

### Instrumentation

Infrared spectra (IR) were collected on a Perkin-Elmer Model 337 spectrophotometer and were calibrated with polystyrene.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on a Bruker AM-250 spectrometer, and the chemical shifts are given in ppm downfield from  $\text{Me}_4\text{Si}$ .  $^{31}\text{P}$  NMR spectra were recorded on the Bruker AM-250, with the chemical shifts being referenced to 85%  $\text{H}_3\text{PO}_4$ . In all cases, deuterated solvents were used to lock the instrument. Electron impact (EI) and fast atom bombardment (FAB) mass spectra were recorded on Kratos MS-30 and VG70-250S spectrometers by Mr. C.R. Weisenberger and Mr. David C. Chang.

### Materials

All solvents were dried and distilled under an Ar atmosphere prior to use: Na/K alloy was used for diethyl ether and hexane, sodium for toluene, potassium benzophenone ketyl for THF and benzene,  $\text{CaH}_2$  for  $\text{CH}_2\text{Cl}_2$ , and  $\text{Mg}(\text{OMe})_2$  for methanol.

Reagents were obtained from various commercial sources and used as received, except as noted below. Tetracyanoethylene (TCNE), from Aldrich, was sublimed, *p*-toluenesulfonyl isocyanate (TSI), also from Aldrich, was distilled at 115°C (2 torr), and  $\text{Co}_2(\text{CO})_8$ , from Strem, was recrystallized from  $\text{CH}_2\text{Cl}_2$  under CO. Literature procedures were used to synthesize  $\text{PhC}\equiv\text{CCH}_2\text{Cl}$  [14],  $[\text{Cp}(\text{CO})_2\text{Ru}]_2$  [15],  $\text{Cp}(\text{PPh}_3)_2\text{RuCl}$  [16],  $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{C}\equiv\text{CPh}$  [12a], and  $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$  [17].

The tosylate  $\text{PhC}\equiv\text{CCH}_2\text{OS}(\text{O})_2\text{C}_6\text{H}_4\text{Me-}p$  was obtained from  $\text{PhC}\equiv\text{CCH}_2\text{OH}$ , *p*- $\text{MeC}_6\text{H}_4\text{S}(\text{O})_2\text{Cl}$ , and KOH by an adaptation of a general literature procedure [18] as a fluffy colorless solid, 74% yield:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.85 (m, Ph),

7.28–7.05 (m, C<sub>6</sub>H<sub>4</sub>), 4.96 (s, CH<sub>2</sub>), 2.39 (s, Me) ppm. Mass spectrum (EI), *m/z* (exact mass): 286.0667 (*M*<sup>+</sup>), C<sub>16</sub>H<sub>14</sub>O<sub>3</sub>S calc. 286.0664 (*M*<sup>+</sup>).

#### Preparation of Cp(CO)<sub>2</sub>RuCH<sub>2</sub>C≡CPh (1)

In a Vacuum Atmospheres drybox under nitrogen, [Cp(CO)<sub>2</sub>Ru]<sub>2</sub> (5.3 g, 12 mmol) was dissolved in 250 ml of THF to give a dark yellow-brown solution. Sodium-potassium alloy (2-fold excess) was added to this solution by pipet, and the resulting suspension was vigorously stirred for 24 h. A mixture of a fine black precipitate and a light yellow-green solution was obtained. The mixture was filtered first through filter paper on a Buchner funnel and then through a fine glass frit to separate the black precipitate. (**Caution:** when removed from the drybox, the filter paper and black precipitate may ignite spontaneously; used filter paper and unreacted Na/K alloy should be treated with methanol.) The solution containing [Cp(CO)<sub>2</sub>Ru]<sup>−</sup> was removed from the drybox, cooled to −78 °C, and PhC≡CCH<sub>2</sub>Cl (2.5 ml, 3.6 g, 24 mmol) was added dropwise via syringe over 10 min with stirring. The solution darkened, and a white precipitate formed within 15 min. After warming to room temperature, the solvent was removed under reduced pressure, and the dark yellow-brown residue was extracted with hexane (2 × 100 ml). The light yellow extracts were combined and filtered through a D-frit. Concentration of the solution induced the precipitation of a light yellow, crystalline product. The remaining solution (~ 10 ml) was removed by cannula, and the solid was dried under vacuum to give **1** (5.7 g) in 70% yield: m.p. 72–75 °C. IR (THF) ν(C≡C) 2182 (w), ν(CO) 2014 (s), 1959 (s) cm<sup>−1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.34–7.16 (m, Ph), 5.33 (s, Cp), 2.17 (s, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 200.7 (s, CO), 130.9 (dt, <sup>1</sup>J(CH) = 161.1 Hz, <sup>2</sup>J(CH) = 6.7 Hz, *p*-C of Ph), 128.1 (dd, <sup>1</sup>J(CH) = 160.3 Hz, <sup>2</sup>J(CH) = 7.4 Hz, *o*-C of Ph), 126.4 (dt, <sup>1</sup>J(CH) = 161.1 Hz, <sup>2</sup>J(CH) = 7.5 Hz, *m*-C of Ph), 125.8 (t, <sup>2</sup>J(CH) = 7.9 Hz, *ipso*-C of Ph), 101.2 (t, <sup>3</sup>J(CH) = 8.0 Hz, ≡C Ph), 89.0 (d of quintets, <sup>1</sup>J(CH) = 178.9 Hz, <sup>2,3</sup>J(CH) = 6.9 Hz, Cp), 81.6 (t, <sup>2</sup>J(CH) = 5.0 Hz, ≡CCH<sub>2</sub>), −26.4 (t, <sup>1</sup>J(CH) = 142.6 Hz, CH<sub>2</sub>) ppm. Mass spectrum (EI), <sup>102</sup>Ru isotope, *m/z*: 338 (*M*<sup>+</sup>), 310 (*M*<sup>+</sup> − CO), 282 (*M*<sup>+</sup> − 2CO), 167 (*M*<sup>+</sup> − 2CO − C<sub>3</sub>H<sub>2</sub>Ph). Anal. Found: C, 56.99; H, 3.21. C<sub>16</sub>H<sub>12</sub>O<sub>2</sub>Ru calc.: C, 56.97; H, 3.59%.

Complex **1** was also obtained by reaction of [Cp(CO)<sub>2</sub>Ru]<sup>−</sup> with PhC≡C-CH<sub>2</sub>OS(O)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Me-*p*. A THF solution (200 ml) of [Cp(CO)<sub>2</sub>Ru]<sup>−</sup> (6.3 mmol) at −78 °C was treated dropwise, with vigorous stirring over 30 min, with 1 equiv. of the tosylate (1.8 g, 6.3 mmol) in 30 ml of THF. The mixture was allowed to warm to room temperature over 2 h, and solvent was removed under vacuum to leave a brown gummy residue. The residue was extracted with hexane (2 × 100 ml, 2 × 50 ml), and the combined extracts were filtered and concentrated to 10 ml to yield 1.2 g (57%) of **1** after decantation and drying.

#### Preparation of Cp(PPh<sub>3</sub>)<sub>2</sub>RuCH<sub>2</sub>C≡CPh (2)

Sublimed Mg (1.0 g, 41 mmol) in 100 ml of diethyl ether was treated with a trace amount of solid HgCl<sub>2</sub> (~ 5 mg), and the clear mixture was gently warmed with a heat gun until it became cloudy (~ 10 s). It was then cooled to 0 °C and treated dropwise, via syringe, with PhC≡CCH<sub>2</sub>Cl (1.0 ml, 10 mmol) over 5 min. The resulting solution was allowed to warm (1 h) and was stirred at room temperature for 10 h. After settling, it was added dropwise, by cannula, over 15 min to 100 ml

of a toluene solution of  $\text{Cp}(\text{PPh}_3)_2\text{RuCl}$  (1.0 g, 1.4 mmol) at  $-78^\circ\text{C}$ . The mixture was allowed to warm to room temperature in 6 h, and solvent was removed from the orange solution under vacuum to leave an orange-red gummy residue. The residue was extracted with toluene ( $2 \times 50$  ml), and the extracts were filtered and concentrated to approx. 10 ml. Addition of 50 ml of hexane induced the precipitation of a light orange solid. The solid was collected on a frit and washed with hexane (10 ml) to yield 0.96 g (87%) of  $\text{Cp}(\text{PPh}_3)_2\text{RuCH}_2\text{C}\equiv\text{CPh}$  (**2**): m.p.  $150^\circ\text{C}$  dec.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.7–7.1 (m, 7Ph), 4.31 (s, Cp), 1.95 (t,  $^3J(\text{PH}) = 12.1$  Hz,  $\text{CH}_2$ ) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  139.7, 135.1, 133.6, 131.9, 130.1, 129.0, 126.5, 125.9 (8m, Ph), 123.5 (t,  $^3J(\text{CH}) = 7.6$  Hz,  $\equiv\text{CPh}$ ), 109.1 (t,  $^2J(\text{CH}) \sim 2$  Hz,  $\equiv\text{CCH}_2$ ), 84.9 (dm, Cp),  $-22.5$  (tt,  $^1J(\text{CH}) = 135$  Hz,  $^2J(\text{PC}) = 11.8$  Hz,  $\text{CH}_2$ ) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  50.09 (s) ppm. Anal. Found: C, 74.29; H, 5.34.  $\text{C}_{50}\text{H}_{42}\text{P}_2\text{Ru}$  calc.: C, 74.52; H, 5.25%.

#### Preparation of $\text{Cp}(\text{CO})_2\text{RuCH}=\text{C}=\text{CH}_2$ (**3**)

By use of the procedure described for **1**, with  $\text{HC}\equiv\text{CCH}_2\text{Cl}$  replacing  $\text{PhC}\equiv\text{CCH}_2\text{Cl}$ , **3** was obtained in 70% yield as an amber liquid. As hexane was removed under reduced pressure, two liquid layers formed, the upper one being hexane and the lower one being **3**. IR (hexane)  $\nu(\text{CO})$  2031 (s), 1984 (s),  $\nu_{\text{as}}(\text{C}=\text{C})$  1917 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.37 (t,  $^4J = 6.4$  Hz, CH), 5.28 (s, Cp), 3.99 (d,  $^4J = 6.4$  Hz,  $\text{CH}_2$ ) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  206.1 (t,  $^2J(\text{CH}) = 3.2$  Hz,  $=\text{C}$ ), 199.5 (s, CO), 88.7 (d of quintets,  $^1J(\text{CH}) = 179$  Hz,  $^{2,3}J(\text{CH}) = 6\text{--}7$  Hz, Cp), 63.1 (dt,  $^1J(\text{CH}) = 166$  Hz,  $^3J(\text{CH}) = 7\text{--}8$  Hz,  $=\text{CH}_2$ ), 58.4 (dt,  $^1J(\text{CH}) = 167$  Hz,  $^3J(\text{CH}) = 9\text{--}10$  Hz,  $=\text{CH}$ ) ppm. Mass spectrum (EI),  $^{102}\text{Ru}$  isotope,  $m/z$ : 262 ( $M^+$ ), 234 ( $M^+ - \text{CO}$ ), 206 ( $M^+ - 2\text{CO}$ ), 167 ( $M^+ - 2\text{CO} - \text{C}_3\text{H}_3$ ).

#### Protonation of $\text{Cp}(\text{CO})_2\text{RuCH}_2\text{C}\equiv\text{CPh}$ (**1**) with $\text{HBF}_4 \cdot \text{OEt}_2$

To a light yellow solution of **1** (0.135 g, 0.40 mmol) in 30 ml of diethyl ether,  $\text{HBF}_4 \cdot \text{OEt}_2$  (85%, 100  $\mu\text{l}$ , 0.60 mmol) was added dropwise at room temperature. Immediately a light cream colored precipitate formed. After 30 min, the colorless solution was removed by cannula, and the solid was washed with diethyl ether ( $2 \times 15$  ml) and dried under vacuum to give an essentially quantitative yield (0.165 g) of [*syn*- $\text{Cp}(\text{CO})_2\text{Ru}(\eta^2\text{-CH}_2=\text{C}=\text{CHPh})\text{BF}_4$ ] (**4a**). IR (Nujol)  $\nu(\text{CO})$  2090 (s), 2059 (s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  7.96 (t,  $^4J = 4.0$  Hz, CH), 7.60–7.50 (m, Ph), 6.19 (s, Cp), 3.70 (d,  $^4J = 4.0$  Hz,  $\text{CH}_2$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  193.6 (CO), 149.0 ( $=\text{C}$ ), 135.7 (*ipso*-C of Ph), 129.6 (*o*-C of Ph), 129.0 (*p*-C of Ph), 128.8 (*m*-C of Ph), 116.7 ( $=\text{CH}$ ), 94.1 (Cp), 14.4 ( $=\text{CH}_2$ ) ppm. Mass spectrum (EI),  $^{102}\text{Ru}$  isotope,  $m/z$ : 338 ( $M^+ - \text{HBF}_4$ ), 282 ( $M^+ - \text{HBF}_4 - 2\text{CO}$ ). Anal. Found: C, 45.29; H, 3.17.  $\text{C}_{16}\text{H}_{13}\text{BF}_4\text{O}_2\text{Ru}$  calc.: C, 45.20; H, 3.08%.

#### Conversion of [*syn*-(**4a**) to [*anti*- $\text{Cp}(\text{CO})_2\text{Ru}(\eta^2\text{-CH}_2=\text{C}=\text{CHPh})\text{BF}_4$ ] (**4b**)

Complex **4a** in acetone- $d_6$  solution at room temperature was monitored by  $^1\text{H}$  NMR spectroscopy. Within 2 h, resonances of **4a** were completely replaced by those of another complex, **4b**. Removal of the solvent afforded pure **4b** as a light cream colored solid: IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu(\text{CO})$  2096 (s), 2053 (s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  7.56–7.52, 7.45–7.30 (2m, Ph), 7.27 (t,  $^4J = 3.9$  Hz, CH), 6.22 (s, Cp), 4.02 (d,  $^4J = 3.9$  Hz,  $\text{CH}_2$ ) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  194.5 (s, CO), 149.7 (d,  $^2J(\text{CH}) = 5.4$  Hz,  $=\text{C}$ ), 135.7 (m, *ipso*-C of Ph), 129.4 (dd,  $^1J(\text{CH}) = 161$  Hz,

$^2J(\text{CH}) = 7.5$  Hz, *o*-C of Ph), 128.5 (dt,  $^1J(\text{CH}) = 162$  Hz,  $^2J(\text{CH}) = 7.2$  Hz, *p*-C of Ph), 127.7 (d of quartets,  $^1J(\text{CH}) = 160$  Hz,  $^2J(\text{CH}) = 7.0$  Hz, *m*-C of Ph), 120.5 (dt,  $^1J(\text{CH}) = 168$  Hz,  $^3J(\text{CH}) < 5$  Hz, =CH), 93.7 (d of quintets,  $^1J(\text{CH}) = 187$  Hz,  $^{2,3}J(\text{CH}) = 6.8$  Hz, Cp), 19.3 (td,  $^1J(\text{CH}) = 173$  Hz,  $^3J(\text{CH}) = 6.5$  Hz, =CH<sub>2</sub>) ppm.

*Reaction of [anti-Cp(CO)<sub>2</sub>Ru(η<sup>2</sup>-CH<sub>2</sub>=C=CHPh)]BF<sub>4</sub> (4b) with Pt(PPh<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)*

A suspension of **4b** (0.43 g, 1.0 mmol) in 60 ml of THF was cooled to  $-78^\circ\text{C}$  and treated with solid Pt(PPh<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>) (0.75 g, 1.0 mmol). The reaction mixture was stirred for 16 h, over which time it was allowed slowly to warm to room temperature. Solvent was removed from a clear yellow solution to give [(η<sup>3</sup>-CH<sub>2</sub>C(Ru(CO)<sub>2</sub>Cp)CHPh)Pt(PPh<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub> (**5**) as a yellow semi-crystalline solid (1.1 g, 96% yield): IR (THF)  $\nu(\text{CO})$  2027 (m-s), 1976 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>)  $\delta$  7.53–7.44, 7.39–7.30, 7.28–7.17, 6.66–6.64 (4m, 7Ph), 5.91 (m, br,  $^2J(\text{PtH}) = 15$  Hz, CH), 5.69 (s, Cp), 4.29 (m,  $^2J(\text{PtH}) = 10$  Hz, *syn* H of CH<sub>2</sub>), 3.48 (dt,  $^3J(\text{PH}) = ^2J = 2.5$  Hz,  $^3J(\text{PH}) = 9.3$  Hz,  $^2J(\text{PtH}) = 39$  Hz, *anti* H of CH<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>)  $\delta$  200.7 (s,  $^3J(\text{PtC}) = 8.8$  Hz, CO), 200.5 (s,  $^3J(\text{PtC}) = 9.3$  Hz, CO), 149.2 (s, *ipso*-C of allyl Ph), 139.5 (d,  $^2J(\text{PC}) = 5.5$  Hz,  $^1J(\text{PtC}) = 38.7$  Hz, CCRu), 135.5–126.5 (m, other C of Ph), 104.7 (d,  $^2J(\text{PC}) = 28.4$  Hz,  $^1J(\text{PtC}) = 123.2$  Hz, CH), 90.9 (s, Cp), 78.4 (d,  $^2J(\text{PC}) = 29.7$  Hz,  $^1J(\text{PtC}) = 106.1$  Hz, CH<sub>2</sub>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>)  $\delta$  17.0 (d,  $^2J(\text{PP}) = 9.3$  Hz,  $^1J(\text{PtP}) = 3850$  Hz), 16.4 (d,  $^2J(\text{PP}) = 9.3$  Hz,  $^1J(\text{PtP}) = 3590$  Hz) ppm. Anal. Found: C, 55.54; H, 4.11. C<sub>52</sub>H<sub>43</sub>BF<sub>4</sub>O<sub>2</sub>P<sub>2</sub>PtRu calc.: C, 54.56; H, 3.79%.

*Reaction of Cp(CO)<sub>2</sub>RuCH<sub>2</sub>C≡CPh (1) with tetracyanoethylene (TCNE)*

Solid TCNE (0.032 g, 0.25 mmol) was added with stirring to a solution of **1** (0.085 g, 0.25 mmol) in 30 ml of benzene at room temperature. The reaction was complete within minutes as ascertained by IR spectroscopy in the  $\nu(\text{CO})$  region. Solvent was removed under reduced pressure to leave the cycloaddition product **6** as a light yellow powder in virtually quantitative yield (0.11 g): m.p. 150°C dec. IR (C<sub>6</sub>H<sub>6</sub>)  $\nu(\text{CO})$  2037 (s), 1989 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.51–7.44, 7.39–7.31 (2m, Ph), 5.18 (s, Cp), 3.65 (s, CH<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)  $\delta$  197.5 (s, CO), 151.3 (=CRu), 134.7 (*ipso*-C of Ph), 131.6, 130.2, 128.3 (other C of Ph), 119.9, 110.5 (CN), 88.2 (Cp), 58.9 (CH<sub>2</sub>), 53.9, 45.2 (C(CN)<sub>2</sub>) ppm. Mass spectrum (EI), <sup>102</sup>Ru isotope, *m/z*: 466 (*M*<sup>+</sup>), 438 (*M*<sup>+</sup> – CO), 410 (*M*<sup>+</sup> – 2CO), 282 (*M*<sup>+</sup> – 2CO – TCNE).

*Reaction of Cp(CO)<sub>2</sub>RuCH<sub>2</sub>C≡CPh (1) with p-toluenesulfonyl isocyanate (TSI)*

A deficiency of TSI (0.13 ml, 0.80 mmol) was added via syringe to a solution of **1** (0.337 g, 1.00 mmol) in 50 ml of CH<sub>2</sub>Cl<sub>2</sub> at room temperature. The resulting light yellow solution was stirred for 16 h, solvent was removed under vacuum, and the residue was washed with hexane (3 × 20 ml) to remove excess **1**. After drying under vacuum, a light yellow powder of the cycloaddition product **7** was obtained (0.22 g, 51% yield). IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu(\text{CO})$  2035 (s), 1987 (s), 1699 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  8.01–7.98, 7.34–7.18 (2m, Ph, C<sub>6</sub>H<sub>4</sub>), 5.08 (s, Cp), 4.57 (s, CH<sub>2</sub>), 2.38 (s, Me) ppm. Anal. Found: C, 53.76; H, 3.77. C<sub>24</sub>H<sub>19</sub>NO<sub>5</sub>RuS calc.: C, 53.93; H, 3.58%.

The reaction of **1** with TSI in CH<sub>2</sub>Cl<sub>2</sub> solution was also studied to determine the rate constant at  $25 \pm 1^\circ\text{C}$ . The IR procedure used was that described in some

detail earlier [19]. Additionally, relative rate constants at 25 °C for the reactions of **1** and  $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{C}\equiv\text{CPh}$  (used as a mixture) with excess TSI in  $\text{CDCl}_3$  solution were measured over 4 h by  $^1\text{H}$  NMR spectroscopy. The ratios of the two metal-propargyl reactants and the two cycloaddition products were determined by integration of the appropriate Cp proton signals.

*Reaction of  $\text{Cp}(\text{CO})_2\text{RuCH}_2\text{C}\equiv\text{CPh}$  (**1**) with  $\text{Co}_2(\text{CO})_8$*

Recrystallized  $\text{Co}_2(\text{CO})_8$  (0.20 g, 0.58 mmol) was added with stirring to a hexane solution (40 ml) of **1** (0.20 g, 0.59 mmol) at 0 °C, and the mixture was allowed to warm to room temperature. The reaction was monitored by IR spectroscopy by following the disappearance of the  $\nu(\text{CO})$  absorption of  $\text{Co}_2(\text{CO})_8$  at  $1858\text{ cm}^{-1}$  and reached completion in 2 h. During this time, the color of the solution changed from light yellow to black. Solvent was removed under vacuum to give black crystalline  $(\text{CO})_3\text{Co}(\mu\text{-}\eta^2\text{-PhC}\equiv\text{CCH}_2\text{Ru}(\text{CO})_2\text{Cp})\text{Co}(\text{CO})_3$  (**8**) (0.35 g, 96% yield): m.p. 136 °C dec. IR (hexane)  $\nu(\text{CO})$  2082 (s), 2041 (s), 2024 (vs), 2018 (sh), 2006 (s), 1973 (s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.55–7.51, 7.41–7.29 (2m, Ph), 5.24 (s, Cp), 3.55 (s,  $\text{CH}_2$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  201.3 (RuCO), 200.7 (br, CoCO), 139.6 (*ipso*-C of Ph), 129.1, 128.6, 127.0 (other C of Ph), 114.7, 92.8 (C $\equiv$ C), 88.3 (Cp), –0.89 ( $\text{CH}_2$ ) ppm. Mass spectrum (EI),  $^{102}\text{Ru}$  isotope,  $m/z$ : 623 ( $M^+ - \text{H}$ ). Anal. Found: C, 42.53; H, 2.06.  $\text{C}_{22}\text{H}_{12}\text{Co}_2\text{O}_8\text{Ru}$  calc.: C, 42.40; H, 1.94%.

*Protonation of  $(\text{CO})_3\text{Co}(\mu\text{-}\eta^2\text{-PhC}\equiv\text{CCH}_2\text{Ru}(\text{CO})_2\text{Cp})\text{Co}(\text{CO})_3$  (**8**) with  $\text{CF}_3\text{CO}_2\text{H}$*

This reaction was conducted similarly to that of the corresponding  $\text{Co}_2\text{Fe}$  complex [4]. After 5 days of stirring at room temperature, a pink precipitate and a brown  $\text{CH}_2\text{Cl}_2$  solution were obtained. The brown solution contained  $(\text{CO})_3\text{Co}(\mu\text{-}\eta^2\text{-PhC}\equiv\text{CMe})\text{Co}(\text{CO})_3$  [20] and unreacted **8**, as shown by  $^1\text{H}$  NMR spectroscopy ( $\delta$  7.55–7.29 (m, Ph), 5.24 (s, Cp), 3.55 (s,  $\text{CH}_2$ ), 2.88 (s, Me) ppm). The pink precipitate revealed a  $^1\text{H}$  NMR signal at  $\delta$  5.46 (s, Cp) ppm in  $\text{CH}_2\text{Cl}_2$  solution.

*Reaction of  $(\text{CO})_3\text{Co}(\mu\text{-}\eta^2\text{-PhC}\equiv\text{CCH}_2\text{Ru}(\text{CO})_2\text{Cp})\text{Co}(\text{CO})_3$  (**8**) with  $\text{PPh}_3$*

Solid  $\text{PPh}_3$  (0.042 g, 0.16 mmol) was added to **8** (0.050 g, 0.080 mmol) dissolved in 20 ml of hexane, and the resulting solution was stirred for 15 h at room temperature. The solution was removed by cannula from a brown-black precipitate, which was then washed with hexane ( $2 \times 10$  ml) and dried under vacuum to give  $(\text{CO})_3\text{Co}(\mu\text{-}\eta^2\text{-PhC}\equiv\text{CCH}_2\text{Ru}(\text{CO})_2\text{Cp})\text{Co}(\text{CO})_2\text{PPh}_3$  (**9**) in 44% yield (0.030 g). IR (THF)  $\nu(\text{CO})$  2059 (s), 2012 (s), 1995 (vs), 1957 (s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.27–7.14 (m, br, 4Ph), 5.14 (s, Cp), 2.93, 2.68 (2d,  $^2J = 10.9$  Hz,  $\text{CH}_2$ ) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  49.8 (s, br) ppm.

*Reaction of  $\text{Cp}(\text{PPh}_3)_2\text{RuCH}_2\text{C}\equiv\text{CPh}$  (**2**) with *p*-toluenesulfonyl isocyanate (TSI)*

A  $\text{CH}_2\text{Cl}_2$  solution (10 ml) of **2** (0.10 g, 0.12 mmol) was treated with an excess of TSI (0.22 ml, 1.5 mmol) dropwise over 5 min at room temperature. The solution changed color from orange to green during the addition. Solvent and excess TSI were then removed under vacuum to give a green solid, which was purified by chromatography on alumina (6%  $\text{H}_2\text{O}$ ) with  $\text{CH}_2\text{Cl}_2$  as eluent, yield 0.085 g (69%) of the cycloaddition product **10**. IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu(\text{CO})$  1740 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.0–6.9 (m, 7Ph,  $\text{C}_6\text{H}_4$ ), 4.12 (s, Cp), 3.48 (s, br,  $\text{CH}_2$ ), 2.42 (s, Me) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  194.2 (m, CO), 167.6 (d,  $^2J(\text{PC}) = 3.5$  Hz, CRu), 142.7 (s, CPh), 136–126 (m, Ph,  $\text{C}_6\text{H}_4$ ), 84.4 (s, Cp), 38.7 (s,  $\text{CH}_2$ ), 21.5 (s, Me)

ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  47.5 (s) ppm. Mass spectrum (FAB),  $^{102}\text{Ru}$  isotope,  $m/z$ : 1004 ( $M^+ + \text{H}$ ), 741 ( $M^+ - \text{PPh}_3$ ), 691 ( $\text{Cp}(\text{PPh}_3)_2\text{Ru}^+$ ), 429 ( $\text{Cp}(\text{PPh}_3)\text{Ru}^+$ ).

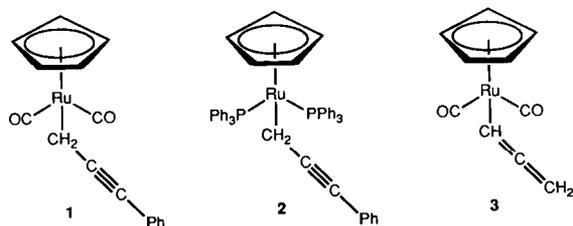
#### Reaction of $\text{Cp}(\text{PPh}_3)_2\text{RuCH}_2\text{C}\equiv\text{CPh}$ (**2**) with $\text{Co}_2(\text{CO})_8$

Freshly recrystallized  $\text{Co}_2(\text{CO})_8$  (0.11 g, 0.32 mmol) was added with stirring to a THF solution (40 ml) of **2** (0.25 g, 0.31 mmol) at room temperature as the solution darkened immediately. A 2-ml aliquot was withdrawn and evaporated to dryness, and the residue was examined by NMR spectroscopy as a  $\text{CDCl}_3$  solution ( $^1\text{H}$  NMR  $\delta$  7.7–6.7 (m, Ph), 4.88 (s, br, Cp), 3.46 (br,  $\text{CH}_2$ ) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR  $\delta$  41.0 (s) ppm). Chromatography of the reaction mixture on a  $20 \times 3$ -cm column of alumina (6%  $\text{H}_2\text{O}$ ) with hexanes as eluent afforded  $(\text{CO})_3\text{Co}(\mu\text{-}\eta^2\text{-PhC}\equiv\text{CMe})\text{Co}(\text{CO})_3$  (0.061 g, 49% yield) after solvent removal from a red band.

## Results and discussion

#### Preparation and characterization of $\text{Cp}(\text{CO})_2\text{RuCH}_2\text{C}\equiv\text{CPh}$ (**1**), $\text{Cp}(\text{PPh}_3)_2\text{RuCH}_2\text{C}\equiv\text{CPh}$ (**2**), and $\text{Cp}(\text{CO})_2\text{RuCH}=\text{C}=\text{CH}_2$ (**3**)

The ruthenium-propargyl complex **1** was obtained in good yield (70%) as a yellow crystalline solid by treatment of a THF solution of  $[\text{Cp}(\text{CO})_2\text{Ru}]^-$  with  $\text{PhC}\equiv\text{CCH}_2\text{Cl}$  at  $-78^\circ\text{C}$  followed by warming to room temperature. Alternatively, the tosylate  $\text{PhC}\equiv\text{CCH}_2\text{OS}(\text{O})_2\text{C}_6\text{H}_4\text{Me-}p$  can be used instead of  $\text{PhC}\equiv\text{CCH}_2\text{Cl}$ , with a somewhat lower isolated yield (57%) of product **1**. The former (and probably also the latter) reaction proceeds substantially, if not completely, at  $-78^\circ\text{C}$  as evidenced by the formation of a white precipitate, presumably  $\text{NaCl}$  and/or  $\text{KCl}$ . Success of this general procedure depends largely on the preparation of a clear solution of the anion  $[\text{Cp}(\text{CO})_2\text{Ru}]^-$ , which is accomplished by reacting  $[\text{Cp}(\text{CO})_2\text{Ru}]_2$  with  $\text{Na/K}$  alloy under a rigorously air-free atmosphere, as described in the Experimental section. The ruthenium- $\eta^1$ -allenyl complex **3** was obtained similarly from  $[\text{Cp}(\text{CO})_2\text{Ru}]^-$  and  $\text{HC}\equiv\text{CCH}_2\text{Cl}$  as an amber liquid, also in 70% yield. Complex **1** decomposes into several unidentified products during attempts at chromatography on alumina (6%  $\text{H}_2\text{O}$ ) or Florisil; complex **3** also undergoes decomposition under these conditions but can be purified, albeit in low yield, by use of a short column. Both **1** and **3** are obtained analytically pure by the procedures detailed in the Experimental section. The two complexes have good solubility in common organic solvents, except in saturated hydrocarbons, in which they are sparingly soluble. Their solutions are sensitive to air, showing signs of decomposition after several minutes of exposure. Compound **1** shows instability toward light and is best stored in the dark under Ar.



The triphenylphosphine-substituted derivative of **1**, **2**, was prepared in high yield (87%) as a light orange solid by reaction of  $\text{Cp}(\text{PPh}_3)_2\text{RuCl}$  with

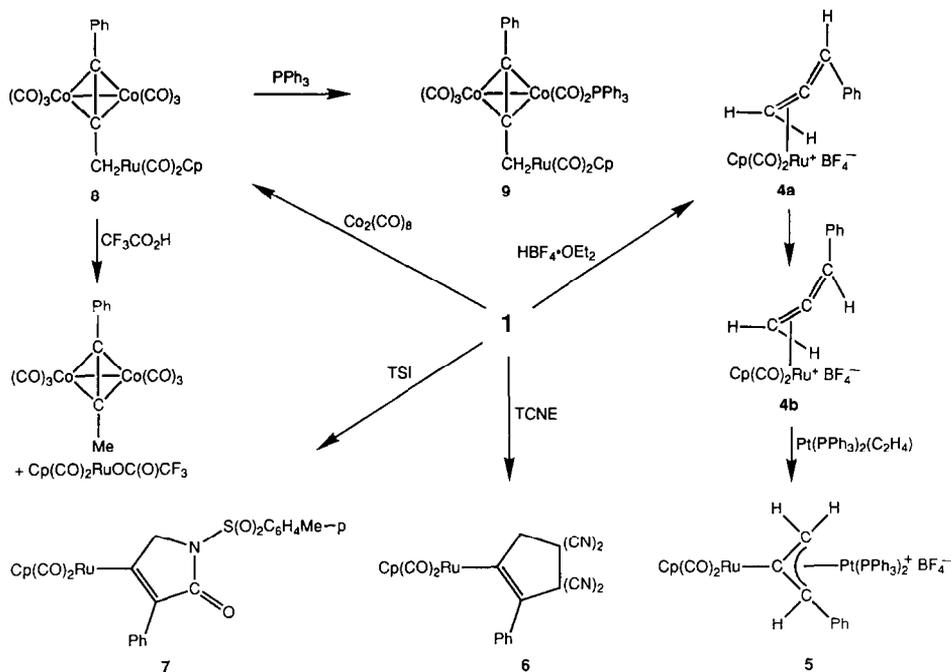
$\text{PhC}\equiv\text{CCH}_2\text{MgCl}$  at  $0^\circ\text{C}$  followed by warming to room temperature. Care needs to be exercised in the preparation of the Grignard reagent (cf. Experimental section), which shows considerable propensity to coupling of the propargyl groups [21]. Solid **2** is stable to air and soluble in benzene, toluene, THF, and  $\text{CH}_2\text{Cl}_2$ . Solutions of **2** decompose in air; the compound is also unstable to chromatography on alumina (6%  $\text{H}_2\text{O}$ ) or Florisil, and it could not be purified in this manner.

The formation of the allenyl **3** instead of a propargyl complex from  $[\text{Cp}(\text{CO})_2\text{Ru}]^-$  and  $\text{HC}\equiv\text{CCH}_2\text{Cl}$  can be rationalized by one of two pathways. The first entails nucleophilic attack of  $[\text{Cp}(\text{CO})_2\text{Ru}]^-$  at the CH carbon of  $\text{HC}\equiv\text{CCH}_2\text{Cl}$  in an  $\text{S}_{\text{N}}2'$  displacement reaction to give the  $\eta^1$ -allenyl ligand directly. The second pathway involves initial formation of  $\text{Cp}(\text{CO})_2\text{RuCH}_2\text{C}\equiv\text{CH}$  followed by its isomerization to **3**. Recently, reaction of  $[\text{Cp}(\text{CO})_3\text{W}]^-$  with  $\text{HC}\equiv\text{CCH}_2\text{Cl}$  at room temperature was shown to give  $\text{Cp}(\text{CO})_3\text{WCH}_2\text{C}\equiv\text{CH}$ , which then underwent rearrangement to  $\text{Cp}(\text{CO})_3\text{WCH}=\text{C}=\text{CH}_2$  [8]. The anion  $[\text{Cp}(\text{CO})_2\text{Ru}]^-$  employed in this study, a much stronger nucleophile than  $[\text{Cp}(\text{CO})_3\text{W}]^-$  [22], reacts with  $\text{HC}\equiv\text{CCH}_2\text{Cl}$  within minutes at  $-78^\circ\text{C}$ . No spectroscopic evidence was obtained for a ruthenium-propargyl precursor in the formation of **3**. The synthesis of **1** and **3** by reaction of  $[\text{Cp}(\text{CO})_2\text{Ru}]^-$  with the respective propargyl chlorides parallels the corresponding chemistry of  $[\text{Cp}(\text{CO})_2\text{Fe}]^-$ , which affords the analogous complexes  $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{C}\equiv\text{CPh}$  and  $\text{Cp}(\text{CO})_2\text{FeCH}=\text{C}=\text{CH}_2$  [12].

Complexes **1–3** were characterized by a combination of elemental analysis, IR and NMR spectroscopy, and mass spectrometry. The IR and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra clearly distinguish between the respective propargyl and allenyl structures of **1** and **3**. Whereas the IR spectrum of **1** shows a weak  $\nu(\text{C}\equiv\text{C})$  band at  $2182\text{ cm}^{-1}$ , that of **3** exhibits a weak  $\nu_{\text{as}}(\text{C}=\text{C}=\text{C})$  absorption at  $1917\text{ cm}^{-1}$ ; each band occurs along with two strong  $\nu(\text{CO})$  absorptions. In the  $^1\text{H}$  NMR spectrum of **1**, the resonance of the  $\text{CH}_2$  protons is observed at  $\delta 2.17\text{ ppm}$ ; for **3**, the  $\text{CH}_2$  group shows a signal farther downfield, at  $\delta 3.99\text{ ppm}$ , as a doublet while the CH group exhibits a resonance at  $\delta 5.37\text{ ppm}$  as a triplet. The four-bond coupling constant,  $^4J$ , of  $6.5\text{ Hz}$  agrees well with that reported for  $\text{Cp}(\text{CO})_2\text{FeCH}=\text{C}=\text{CH}_2$  ( $6.5\text{ Hz}$ ) [12a,c] and  $\text{Cp}(\text{CO})_3\text{WCH}=\text{C}=\text{CH}_2$  ( $6.7\text{ Hz}$ ) [8]. In the  $^{13}\text{C}$  NMR spectra, the resonance of the  $\text{CH}_2$  carbon of **3** ( $\delta 63.1\text{ ppm}$ ) also occurs considerably downfield from that of the corresponding carbon of **1** ( $\delta -26.4\text{ ppm}$ ), as observed recently for  $\text{Cp}(\text{CO})_3\text{WCH}=\text{C}=\text{CH}_2$  and  $\text{Cp}(\text{CO})_3\text{WCH}_2\text{C}\equiv\text{CH}$  [8]. The values of  $^1J(\text{CH})$  for the  $\text{CH}_2$  group of **1** and **3** ( $142.6$  and  $166\text{ Hz}$ , respectively) are compatible with the expected different hybridization at that carbon in the two complexes. The signal of the central carbon of the allenyl ligand of **3** is observed considerably downfield at  $\delta 206.1\text{ ppm}$ , close to the corresponding signal of  $\text{Cp}(\text{CO})_3\text{WCH}=\text{C}=\text{CH}_2$  ( $\delta 209.1\text{ ppm}$ ).

Interestingly, the EI mass spectra of **1** and **3** show similar fragmentation patterns, i.e. stepwise loss of CO and then of the  $\sigma$ -hydrocarbon group. This may be contrasted with the different fragmentation patterns of  $\text{Cp}(\text{CO})_3\text{WCH}_2\text{C}\equiv\text{CH}$  and  $\text{Cp}(\text{CO})_3\text{WCH}=\text{C}=\text{CH}_2$ , the former showing that the primary cleavage occurs at the W–propargyl bond and the latter that it occurs at the W–CO bond [8]. It is possible that the Ru–propargyl and Ru–allenyl bonds are closer in energy than the corresponding bonds of the tungsten complexes.

The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of **2** exhibit features similar to those noted for the unsubstituted propargyl complex **1**. Thus, the  $^1\text{H}$  and  $^{13}\text{C}$  resonances of the



Scheme 1

CH<sub>2</sub> group are observed, now as triplets, at  $\delta$  1.95 ppm ( $^3J(\text{PH}) = 12.1$  Hz) and  $\delta$  -22.5 ppm ( $^2J(\text{PC}) = 11.8$  Hz), respectively. The signals of the C $\equiv$ C carbons of **2** at  $\delta$  123.5 and 109.1 ppm may be compared with the corresponding signals of **1** at  $\delta$  101.2 and 81.6 ppm. No <sup>13</sup>C NMR signals are discernible downfield from those of the phenyl carbons ( $\delta > 140$  ppm). A signal at  $\delta \sim 200$  ppm would be expected for a Ru- $\eta^1$ -allenyl complex.

### Reactions of Cp(CO)<sub>2</sub>RuCH<sub>2</sub>C $\equiv$ CPh (**1**)

Reactions of **1** and of some of its products are set out in Scheme 1. Addition of HBF<sub>4</sub>·OEt<sub>2</sub> to a diethyl ether solution of **1** at room temperature results in the immediate precipitation of a light cream colored solid, which is formulated as the BF<sub>4</sub><sup>-</sup> salt of the ruthenium- $\eta^2$ -allene cationic complex, **4a**. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR measurements on a freshly prepared acetone-*d*<sub>6</sub> solution of this complex reveal a mixture of two isomers; however, within 2 h only one isomer, **4b**, remains. Isomer **4a** is assigned a *syn* structure, in which the ruthenium and the Ph group are on the same side of the  $\eta^2$ -allene ligand. The thermodynamically more stable isomer, **4b**, is thought to adopt an *anti* structure, with the metal and the Ph group on the opposite sides of the  $\eta^2$ -allene ligand. The situation is analogous to that reported for the protonation of Cp(CO)<sub>2</sub>FeCH<sub>2</sub>C $\equiv$ CMe, which initially affords [*syn*-Cp(CO)<sub>2</sub>Fe( $\eta^2$ -CH<sub>2</sub>=C=CHMe)]<sup>+</sup>; on warming to 50°C in nitromethane, this complex attains equilibrium with its *anti* isomer [23]. Similar protonation of Cp(CO)<sub>2</sub>FeCH<sub>2</sub>C $\equiv$ CPh gave only one isomer of the corresponding iron- $\eta^2$ -allene cation, but it has not been established whether this isomer is *syn* or rearranged *anti* [24,25].

Complexes **4a** and **4b** show similar IR and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, which closely resemble those of  $[\text{Cp}(\text{CO})_2\text{Fe}(\eta^2\text{-CH}_2\text{=C=CHPh})]^+$  [25]. The proton signals of the CH and  $\text{CH}_2$  groups are observed at  $\delta$  7.96 and 3.70 (*syn*) ppm and  $\delta$  7.27 and 4.02 (*anti*) ppm, respectively, with a coupling constant,  $^4J$ , of 4.0 (*syn*) and 3.9 Hz (*anti*). These values of  $^4J$  are appreciably lower than those for free allenes (6–7 Hz) [26] owing to nonlinearity of the  $\eta^2$ -allene fragment [27]. The values of  $^1J(\text{CH})$ , obtained from the  $^{13}\text{C}$  NMR spectrum of **4b**, are 168 (CH) and 173 Hz ( $\text{CH}_2$ ), indicative of  $sp^2$  hybridization at these carbon atoms.

Attempts to protonate **1** with  $\text{CF}_3\text{CO}_2\text{H}$  and an ethereal solution of HCl under the conditions similar to those for  $\text{HBF}_4 \cdot \text{OEt}_2$  proved unsuccessful. Trifluoroacetic acid showed no apparent reaction, and HCl yielded a yellow precipitate of  $\text{Cp}(\text{CO})_2\text{RuCl}$  [28].

In an effort to synthesize a bimetallic RuPt complex, we carried out a reaction of **4b** with  $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$  at  $-78^\circ\text{C}$  with warming to room temperature. This experiment is predicated on Powell's synthesis of  $[(\eta^3\text{-CH}_2\text{C}(\text{Fe}(\text{CO})(\text{PR}_3)\text{-Cp})\text{CH}_2)\text{Pt}(\text{PPh}_3)_2]^+$  from  $[\text{Cp}(\text{CO})(\text{PR}_3)\text{Fe}(\eta^2\text{-CH}_2\text{=C=CH}_2)]^+$  ( $\text{PR}_3 = \text{PPh}_2\text{H}$ ,  $\text{PPhMe}_2$ ) and  $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$  [29]. An essentially quantitative yield was obtained of a yellow solid, formulated as **5** on the basis of analytical data and a comparison of spectroscopic data with those of Powell's products, the structure of one of which ( $\text{PR}_3 = \text{PPhMe}_2$ ) was elucidated by X-ray crystallography. It is noteworthy that the conversion of **4b** by  $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$  to **5** may be regarded as a redox reaction in which the allene is formally reduced to a ruthenium-substituted allyl anion while platinum(0) is oxidized to platinum(II). The positive charge of **5** is largely localized on the platinum part of the complex, as reflected by the much lower values of  $\nu(\text{CO})$  for **5** (2027, 1976  $\text{cm}^{-1}$ ) than of the precursor **4b** (2096, 2053  $\text{cm}^{-1}$ ). The former numbers are only slightly higher than those for the neutral **1** (2014, 1959  $\text{cm}^{-1}$ ).

The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of **5** demonstrate that only one isomer is present. The allylic carbon resonances occur at  $\delta$  139.5 (CRu), 104.7 (CH), and 78.4 ( $\text{CH}_2$ ) ppm with the respective platinum-carbon coupling constants,  $^1J(\text{PtC})$ , of 38.7, 123.3, and 106.1 Hz, in agreement with the proposed structure [29]. The  $^1\text{H}$  NMR signals of the allyl group at  $\delta$  5.91, 4.29, and 3.48 ppm are assigned to the CH, *syn* H of  $\text{CH}_2$ , and *anti* H of  $\text{CH}_2$ , respectively. These assignments are based on a comparison with the corresponding data for the related FePt complexes [29], on the generally observed more upfield chemical shifts of the allyl *anti* than *syn* protons [29,30], and on the values of the coupling constants  $^2J(\text{PtH})$ : 15 (CH), 10 (*syn* H of  $\text{CH}_2$ ), and 39 Hz (*anti* H of  $\text{CH}_2$ ). Since allylic *anti* hydrogens show a considerably larger  $^2J(\text{PtH})$  than do the *syn* hydrogens [31], we assign the signal at  $\delta$  5.91 ppm to the *CHPh* proton in a *syn* position. Accordingly, **5** is formulated as the *anti* isomer. This assignment implies that the conversion of **4b** to **5** occurred with retention of configuration about the  $=\text{CHPh}$  carbon with respect to the bent  $\text{C}_3$  fragment.

The reaction in point could proceed by replacement of the ethylene in  $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$  with the  $\text{C=CHPh}$  double bond of **4b** [29]. Alternatively, however, it can be initiated by nucleophilic attack of platinum(0) at the  $\text{CH}_2$  carbon of **4b** in a process that is analogous to the known addition reactions of nucleophiles to coordinated  $\eta^2$ -allene [25].

Like other metal-propargyl complexes [2,19,32], **1** undergoes facile [3 + 2] cy-

Table 1

Bimolecular rate constants ( $k_2$ ) for the reaction of  $\text{Cp}(\text{CO})_x\text{MCH}_2\text{C}\equiv\text{CPh}$  with TSI in  $\text{CH}_2\text{Cl}_2$  at  $25 \pm 1^\circ\text{C}$

Complex		$10^3 k_2^a$ ( $M^{-1} s^{-1}$ )	Reference
M	x		
Ru	2	2.7	This work
Fe	2	2.1	19
Mo	3	0.70	19
W	3	0.27	19

<sup>a</sup>  $\pm 10\%$  or better

claddition reactions with TCNE and TSI. The products **6** and **7**, respectively, were isolated as yellow solids that are stable to air. They were characterized by a combination of elemental analysis, IR and  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  spectroscopy, and mass spectrometry. The spectroscopic data for **6** and **7** — especially  $^{13}\text{C}\{^1\text{H}\}$  NMR data for **6** — show close similarities to those of analogous [3 + 2] cycloadducts [19,32,33].

To ascertain how reactivity of the ruthenium complex **1** toward these electrophilic reagents compares with that of other metal propargyls, the reaction of **1** with TSI was carefully monitored by IR spectroscopy at  $25 \pm 1^\circ\text{C}$ . In Table 1, the bimolecular rate constant ( $2.7 \times 10^{-3} M^{-1} s^{-1}$ ),  $k_2$ , obtained from the IR data is compared with that for the reactions of other  $\text{Cp}(\text{CO})_x\text{MCH}_2\text{C}\equiv\text{CPh}$  complexes with TSI under similar conditions [19]. Complex **1** is only slightly more reactive (1.3 times) than its iron counterpart,  $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{C}\equiv\text{CPh}$ . This ratio of the rate constants was confirmed by  $^1\text{H}$  NMR spectroscopy. By following the reaction of a mixture of **1** and  $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{C}\equiv\text{CPh}$  with an excess of TSI at  $25^\circ\text{C}$ , an approximate ratio of the rate constants,  $k_2(\text{Ru})/k_2(\text{Fe}) \sim 1.4$ , was obtained.

Another common reaction of transition-metal propargyls is that with  $\text{Co}_2(\text{CO})_8$  [4,5]. This reaction, an extension of the chemistry of acetylenes and  $\text{Co}_2(\text{CO})_8$  [34], results in the replacement of the bridging carbonyls with the propargylic  $\text{C}\equiv\text{C}$ . Complex **1**, like the congeneric iron propargyl  $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{C}\equiv\text{CPh}$  [4], readily reacts with  $\text{Co}_2(\text{CO})_8$  to give a trinuclear metal product, **8**, as a black, air-stable solid in virtually quantitative yield.

Product **8** was characterized by elemental analysis and by comparison of its spectroscopic data with those of  $(\text{CO})_3\text{Co}(\mu\text{-}\eta^2\text{-PhC}\equiv\text{CCH}_2\text{Fe}(\text{CO})_2\text{Cp})\text{Co}(\text{CO})_3$ . The chemical shifts of the  $\text{C}\equiv\text{C}$  and  $\text{CH}_2$  carbons in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of the two trinuclear products are very similar:  $\delta$  114.7, 92.8, and  $-0.89$  ppm for **8** and  $\delta$  114.0, 93.5, and 6.1 ppm for its  $\text{Co}_2\text{Fe}$  analogue [4], respectively. These resonances of **8** are shifted downfield compared to those of the parent propargyl complex **1**.

Like its iron counterpart (but unlike the  $\text{Cp}(\text{CO})_3\text{Mo}$  and  $-\text{W}$  analogues) [4], **8** can be chromatographed on alumina with only minor decomposition. It is, however, much less reactive toward  $\text{CF}_3\text{CO}_2\text{H}$  than the  $\text{Co}_2\text{Fe}$  complex. Whereas the latter undergoes complete cleavage of the  $\text{Fe}-\text{CH}_2$  bond within 18 h at room temperature [4], the former affords only a partial conversion to  $(\text{CO})_3(\mu\text{-}\eta^2\text{-PhC}\equiv\text{CMe})\text{Co}(\text{CO})_3$  and presumably  $\text{Cp}(\text{CO})_2\text{RuOC}(\text{O})\text{CF}_3$  (formulated by comparison of the  $^1\text{H}$  NMR spectrum with that of  $\text{Cp}(\text{CO})_2\text{FeOC}(\text{O})\text{CF}_3$  [35]) under comparable conditions in 5 days. The observed relative reactivities of **8** and its

Co<sub>2</sub>Fe analogue are consistent with the more facile electrophilic cleavage of the Fe–C bonds than of the Ru–C bonds in analogous alkyl complexes Cp(CO)<sub>2</sub>MR [36].

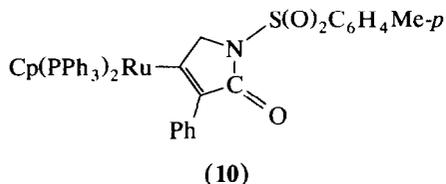
Complex **8** reacts with PPh<sub>3</sub> at room temperature to yield a monosubstituted product, **9**. That the substitution occurred at one of the cobalt atoms is evidenced by the appearance of a broad <sup>31</sup>P{<sup>1</sup>H} NMR signal at δ 49.8 ppm. This broadening can be ascribed to quadrupolar coupling with the <sup>59</sup>Co nucleus [37]. In the <sup>1</sup>H NMR spectrum of **9**, the CH<sub>2</sub> protons are inequivalent, giving rise to two broad doublets (an AB pattern) at δ 2.93 and 2.68 ppm with a geminal proton–proton coupling constant of 10.9 Hz, characteristic of diastereotopic hydrogens of an *sp*<sup>3</sup> CH<sub>2</sub> group [38]. In addition, the chemical shift of the Cp protons is only slightly affected by the substitution (δ 5.14 ppm for **8** versus δ 5.24 ppm for **9**), providing further evidence that PPh<sub>3</sub> is bonded to Co rather than Ru.

The propargyl **1** readily reacts with Fe<sub>2</sub>(CO)<sub>9</sub> to afford a variety of heteronuclear iron-ruthenium complexes [7]. The extensive chemistry of this system will be published separately [39].

#### Reactions of Cp(PPh<sub>3</sub>)<sub>2</sub>RuCH<sub>2</sub>C≡CPh (**2**)

Reactions between **2** and several substrates were investigated to determine what effect replacement of the two carbonyl groups in **1** with PPh<sub>3</sub> would have on reactivity. Not unexpectedly, it was observed that **2** reacts with electrophiles much more rapidly than does **1**; however, its reactions tend to be complicated by dissociation of PPh<sub>3</sub>, and products are generally less stable and more difficult to purify than those derived from **1**. As a result, limited success was achieved with this aspect of our investigation. Only the more definitive findings are included in this paper.

The propargyl **2** reacts rapidly with TSI to afford the expected [3 + 2] cycloadduct **10**. From qualitative observations, this reaction proceeds at least as fast



as that of (CO)<sub>4</sub>(PPh<sub>3</sub>)MnCH<sub>2</sub>C≡CMe, which is more than 75 times faster than the corresponding reaction of **1** [19]. The isolated green solid was characterized as **10** by IR and NMR spectroscopy and mass spectrometry. Thus, the IR spectrum shows a lactam ν(CO) band at 1740 cm<sup>-1</sup>, and the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum displays resonances of the ring carbons at δ 194.2 (CO), 167.6 (CRu), 142.7 (CPh), and 38.7 (CH<sub>2</sub>) ppm. These values are in good agreement with those reported for other [3 + 2] cycloadducts of metal-propargyl complexes and organic isocyanates [19,34]. The FAB mass spectrum of **10** adds further support to the proposed formulation. The fragmentation patterns involve ions that derive from loss of PPh<sub>3</sub> and the lactam ring by the molecular ion.

Complex **2** also reacts very rapidly with Co<sub>2</sub>(CO)<sub>8</sub>. The <sup>1</sup>H NMR spectrum of the reaction solution accords with the presence of a trinuclear Co<sub>2</sub>Ru complex that is structurally analogous to **8** but contains a Cp(PPh<sub>3</sub>)<sub>2</sub>Ru group instead of

$\text{Cp}(\text{CO})_2\text{Ru}$ . The product decomposed during purification by chromatography, and only  $(\text{CO})_3\text{Co}(\mu\text{-}\eta^2\text{-PhC}\equiv\text{CMe})\text{Co}(\text{CO})_3$  could be isolated after workup.

Reaction of **2** with  $\text{Fe}_2(\text{CO})_9$  in THF at room temperature proceeds differently from the corresponding reaction of **1** [7]. No heteronuclear metal complexes were observed, and only products of exchange of CO and  $\text{PPh}_3$  were apparently obtained. These products are  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{RuCH}_2\text{C}\equiv\text{CPh}$  and  $\text{Fe}(\text{CO})_4\text{PPh}_3$  [40]. The new ruthenium-propargyl complex was formulated on the basis of spectroscopic data, which include an IR  $\nu(\text{CO})$  band at  $1916\text{ cm}^{-1}$  (in THF),  $^1\text{H}$  NMR signals at  $\delta$  4.92 (Cp) and 2.55 (br,  $\text{CH}_2$ ) ppm,  $^{13}\text{C}\{^1\text{H}\}$  resonances at  $\delta$  217.8 (CO), 169.2 ( $\equiv\text{CPh}$ ), 150.5 ( $\equiv\text{CCH}_2$ ), 90.6 (Cp), and 15.2 ( $\text{CH}_2$ ) ppm, and a  $^{31}\text{P}\{^1\text{H}\}$  resonance at  $\delta$  41.0 ppm (all in  $\text{CDCl}_3$ ). The same complex was obtained by reaction of **2** with CO at room temperature. The reaction of **2** with  $\text{Fe}_2(\text{CO})_9$  is strictly analogous to that between  $\text{Cp}(\text{PPh}_3)_2\text{RuCl}$  and  $\text{Fe}_2(\text{CO})_9$ , which leads to the formation of  $\text{Cp}(\text{CO})(\text{PPh}_3)\text{RuCl}$  and  $\text{Fe}(\text{CO})_4\text{PPh}_3$  [16]. Because of the propensity of **2** to undergo facile CO substitution, no further reactions of this propargyl complex with metal carbonyls were investigated.

### Acknowledgements

We gratefully acknowledge financial support of the National Science Foundation and The Ohio State University. Mass spectra were obtained at The Ohio State University Chemical Instrument Center (funded in part by National Science Foundation Grant 79-10019). We also thank the Johnson Matthey Co. for a loan of ruthenium trichloride.

### References

- 1 A. Wojcicki and C.E. Shuchart, *Coord. Chem. Rev.*, 105 (1990) 35.
- 2 A. Wojcicki, in M. Tsutsui, Y. Ishii and Y. Huang (Eds.), *Fundamental Research in Organometallic Chemistry*, Van Nostrand-Reinhold, New York, 1982, pp. 569–597.
- 3 M. Rosenblum, *Acc. Chem. Res.*, 7 (1974) 122.
- 4 T.M. Wido, G.H. Young, A. Wojcicki, M. Calligaris and G. Nardin, *Organometallics*, 7 (1988) 452.
- 5 G.H. Young and A. Wojcicki, *J. Organomet. Chem.*, 390 (1990) 351.
- 6 (a) G.H. Young, A. Wojcicki, M. Calligaris, G. Nardin and N. Bresciani-Pahor, *J. Am. Chem. Soc.*, 111 (1989) 6890; (b) G.H. Young, M.V. Raphael, A. Wojcicki, M. Calligaris, G. Nardin and N. Bresciani-Pahor, *Organometallics*, 10 (1991) 1934.
- 7 C.E. Shuchart, G.H. Young, A. Wojcicki, M. Calligaris and G. Nardin, *Organometallics*, 9 (1990) 2417.
- 8 R.-S. Keng and Y.-C. Lin, *Organometallics*, 9 (1990) 289.
- 9 J.L. Davidson, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, Vol. 4, Pergamon Press, Oxford, 1982, Chap. 31.5.
- 10 M.A. Bennett, M.I. Bruce and T.W. Matheson, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, Vol. 4, Pergamon Press, Oxford, 1982, Chap. 32.4.
- 11 M.A. Bennett and T.W. Matheson, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, Vol. 4, Pergamon Press, Oxford, 1982, Chap. 32.9.
- 12 (a) J.-L. Roustan and P. Cadot, *C. R. Acad. Sci., Ser. C*, 268 (1969) 734; (b) M.D. Johnson and C. Mayle, *Chem. Commun.*, (1969) 192; (c) P.W. Jolly and R. Pettit, *J. Organomet. Chem.*, 12 (1968) 491; (d) J.K.P. Ariyaratne and M.L.H. Green, *J. Organomet. Chem.*, 1 (1964) 90.
- 13 D.F. Shriver and M.A. Drezdson, *The Manipulation of Air-Sensitive Compounds*, 2nd ed., Wiley, New York, 1986.
- 14 J.D. Slagle, T.S. Huang and G. Franzus, *J. Org. Chem.*, 46 (1981) 3526.

- 15 N.M. Doherty and S.A.R. Knox, *Inorg. Synth.*, 25 (1989) 179.
- 16 T. Blackmore, M.I. Bruce and F.G.A. Stone, *J. Chem. Soc. A*, (1971) 2376.
- 17 D.M. Blake and D.M. Roundhill, *Inorg. Synth.*, 18 (1980) 120.
- 18 L. Brandsma and H.D. Verkruijsse, *Synthesis of Acetylenes, Allenes, and Cumulenes*, Elsevier, New York, 1981, pp. 223–224
- 19 P.B. Bell and A. Wojcicki, *Inorg. Chem.*, 20 (1981) 1585.
- 20 G. Cetani, O. Gambino, R. Rossetti and E. Sappa, *J. Organomet. Chem.*, 8 (1967) 149
- 21 M.S. Kharash and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Vol. 1, Prentice Hall, New York, 1954, Chap. 1.
- 22 R.E. Dessy, R.L. Pohl and R.B. King, *J. Am. Chem. Soc.*, 88 (1966) 5121
- 23 (a) S. Raghu and M. Rosenblum, *J. Am. Chem. Soc.*, 95 (1973) 3060; (b) B. Foxman, D. Marten, A. Rosan, S. Raghu and M. Rosenblum, *J. Am. Chem. Soc.*, 99 (1977) 2160.
- 24 J. Benaim, J.-Y. Méroux and J.-L. Roustan, *C. R. Acad. Sci., Ser. C*, 272 (1971) 289.
- 25 (a) D.W. Lichtenberg and A. Wojcicki, *J. Am. Chem. Soc.*, 94 (1972) 8271; (b) D.W. Lichtenberg and A. Wojcicki, *J. Organomet. Chem.*, 94 (1975) 311.
- 26 L.M. Jackman and S. Sternhell, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed., Pergamon Press, New York, 1969, pp. 328–330.
- 27 B.M. Foxman, *J. Chem. Soc., Chem. Commun.*, (1975) 221
- 28 T. Blackmore, J.D. Cotton, M.I. Bruce and F.G.A. Stone, *J. Chem. Soc. A*, (1968) 2931
- 29 M.R. Gregg, J. Powell and J.F. Sawyer, *J. Organomet. Chem.*, 352 (1988) 357
- 30 G. Carturan, A. Scriveri, B. Longato and F. Morandini, *J. Organomet. Chem.*, 172 (1979) 91
- 31 B.E. Mann, B.L. Shaw and G. Shaw, *J. Chem. Soc. A*, (1971) 3536
- 32 S.R. Su and A. Wojcicki, *Inorg. Chim. Acta*, 8 (1974) 55
- 33 J.P. Williams and A. Wojcicki, *Inorg. Chem.*, 16 (1977) 2506.
- 34 R.S. Dickson and P.J. Fraser, *Adv. Organomet. Chem.*, 12 (1974) 323
- 35 R.B. King and R.N. Kapoor, *J. Organomet. Chem.*, 15 (1968) 457.
- 36 S.E. Jacobson and A. Wojcicki, *J. Organomet. Chem.*, 72 (1974) 113.
- 37 S. Aime, L. Milone and M. Valle, *Inorg. Chim. Acta*, 18 (1976) 9
- 38 L.M. Jackman and S. Sternhell, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed., Pergamon Press, New York, 1969, Chap. 4-1.
- 39 C.E. Shuchart, M. Calligaris, P. Faleschini and A. Wojcicki, in preparation
- 40 A.F. Clifford and A.K. Mukherjee, *Inorg. Chem.*, 2 (1963) 151