# Formation and reactivity of the zirconium ethylene complexes $[\eta^5-C_5H_3-1,3-(SiMe_2CH_2PR_2)_2]Zr(\eta^2-CH_2=CH_2)(X)$ (R = Me, Pr<sup>*i*</sup>; X = Br, C<sub>5</sub>H<sub>5</sub>)

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**Abstract**: The formation and reactivity of the zirconium ethylene complexes  ${}^{R}[P_{2}Cp]Zr(\eta^{2}-CH_{2}=CH_{2})(X)$  (**2a**:  $R = Pr^{i}$ , X = Br; **2b**: R = Me, X = Br; **4a**:  $R = Pr^{i}$ ,  $X = C_{5}H_{5}$ ;  ${}^{R}[P_{2}Cp] = (\eta^{5}-C_{5}H_{3}-1,3-(SiMe_{2}CH_{2}PR_{2})_{2}))$  are described. Ethylene complexes **2a** and **2b** are prepared from a reaction of  ${}^{R}[P_{2}Cp]ZrCl_{3}$  (**1a**:  $R = Pr^{i}$ ; **1b**: R = Me) with 2 equiv of EtMgBr, presumably via β-H elimination from the diethyl intermediate  ${}^{R}[P_{2}Cp]ZrCl(CH_{2}CH_{3})_{2}$ . The structure of **2b** was determined by X-ray crystallography. Addition of carbon monoxide to 16-electron **2** displaces the ethylene ligand to generate the carbonyl complex  ${}^{R}[P_{2}Cp]Zr(CO)_{2}Br$  (**5a**:  $R = Pr^{i}$ ; **5b**: R = Me), which is stable only under an atmosphere of CO. The corresponding CO reaction with 18-electron **4a** to give the metallocene monocarbonyl analogue  ${}^{Pr}[P_{2}Cp]Zr(\eta^{5}-C_{5}H_{5})(CO)$  (**6a**) is considerably slower. **2a** exhibits fluxional exchange of one carbonyl ligand with bulk  ${}^{13}CO$  in solution; the kinetic parameters for this exchange process are  $\Delta H^{\ddagger} = 9.2(5)$  kcal mol<sup>-1</sup> and  $\Delta S^{\ddagger} = -17(2)$  cal mol<sup>-1</sup> K<sup>-1</sup>. The addition of diphenylacetylene to **2a** yields the alkyne complex  ${}^{Pr}[P_{2}Cp]Zr(\eta^{2}-PhCCPh)Br$  (**7a**), which exists in solution as two isomers in equilibrium. A solid-state X-ray structure determination for the minor isomer *syn-***7a** was performed.

Key words: zirconium, cyclopentadienyl phosphine, alkyne, metallocyclopropane.

**Résumé** : On décrit la formation et la réactivité de complexes de l'éthylène zirconium  ${}^{R}[P_{2}Cp]Zr(\eta^{2}-CH_{2}=CH_{2})(X)$ (**2a** : R = *i*Pr, X = Br; **2b** : R = Me, X = Br; **4a** : R = *i*Pr, X = C<sub>5</sub>H<sub>5</sub>;  ${}^{R}[P_{2}Cp] = (\eta^{5}-C_{5}H_{3}-1,3-(SiMe_{2}CH_{2}PR_{2})_{2}))$ . On a préparé les complexes **2a** et **2b** par réaction du  ${}^{R}[P_{2}Cp]ZrCl_{3}$  (**1a** : R = *i*Pr; **1b** : R = Me) avec deux équivalents de EtMgBr, probablement par le biais d'une élimination  $\beta$  d'hydrogène à partir de l'intermédiaire diéthylé  ${}^{R}[P_{2}Cp]ZrCl(CH_{2}CH_{3})_{2}$ . On a déterminé la structure du complexe **2b** par diffraction des rayons X. L'addition de monoxyde de carbone au complexe **2** à seize électrons conduit à un déplacement du ligand éthylène et à la formation du complexe carbonylé  ${}^{R}[P_{2}Cp]Zr(CO)_{2}Br$  (**5a**: R = *i*Pr; **5b**: R = Me) qui n'est stable que sous une atmosphère de CO. La réaction correspondante du CO avec le complexe **4a** à dix-huit électrons, qui conduit à la formation du métallocène monocarbonylé analogue,  ${}^{R}[P_{2}Cp]Zr(\eta^{5}-C_{5}H_{5})(CO)$  (**6a**) est beaucoup plus lente. Le complexe **2a** donne lieu à un échange fluxionnel d'un ligand carbonyle avec le  ${}^{13}CO$  qui se trouve dans l'ensemble de la solution; les paramètres cinétiques pour ce processus d'échange sont  $\Delta H^{\ddagger}$ . = 9,2(5) kcal mol<sup>-1</sup> et  $\Delta S^{\ddagger}$  = -17,2 cal mol<sup>-1</sup> K<sup>-1</sup>. L'addition de diphénylacétylène au complexe **2a** conduit à la formation de  ${}^{R}[P_{2}Cp]Zr(\eta^{2}-PhCCPh)Br$  (**7a**) qui, en solution, existe sous la forme de deux isomères à l'équilibre. Faisant appel à la diffraction des rayons X, on a effectué une détermination de la structure en phase solide de l'isomère mineur, le *syn-7a*.

Mots clés : zirconium, cyclopentadiényl phosphine, alcyne, métallocyclopropane.

[Traduit par la Rédaction]

### Introduction

The coordination of ethylene to transition metal centers is one of the foundations of organometallic chemistry (1) and dates back to the synthesis of Zeise's salt (K[Pt( $\eta^2$ -CH<sub>2</sub>=CH<sub>2</sub>)Cl<sub>3</sub>]) in 1827. Currently, the chemistry of metalalkene complexes encompasses numerous important catalytic industrial processes, such as alkene polymerization using Ziegler–Natta catalysts, olefin metathesis (2, 3) (which includes both ring-opening (4) and ring-closing (5) metathesis type processes), alkene hydrogenation (6), and the Wacker process (7). In addition, there is continued interest in the bonding aspects of the metal-alkene interaction (8), which has been the focus of theoretical studies (9).

Received September 5, 2000. Published on the NRC Research Press Web site at http://canjchem.nrc.ca on May 23, 2001.

Dedicated to Professor B. R. James, in recognition of his distinguished contributions to homogeneous catalysis, on the occasion of his 65th birthday.

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We have been examining the reactivity of zirconium complexes stabilized by the hybrid donor ancillary ligand  $\eta^5$ - $C_5H_3$ -(SiMe<sub>2</sub>CH<sub>2</sub>PR<sub>2</sub>)<sub>2</sub> (<sup>R</sup>[P<sub>2</sub>Cp], R = Pr<sup>i</sup>, Me). Deployment of bulky isopropyl substituents on the side-arm phosphines has enabled the isolation of Zr(IV) alkylidene complexes, Pr[P<sub>2</sub>Cp]Zr=CHR(Cl), (10, 11) from which reaction with ethylene yields the ethylene adduct  $\Pr[P_2Cp]Zr(\eta^2-CH_2=CH_2)Cl$ (2c) (11). An interest in studying the reactivity of this product as a probe into the nature of the metal-alkene bonding in this formally Zr(II) species led to a more direct synthetic route from the starting chloride <sup>Pr</sup>[P<sub>2</sub>Cp]ZrCl<sub>3</sub> (1a). One advantage of this alternate preparation is the ability to obtain the analogous but less bulky Me[P<sub>2</sub>Cp]Zr ethylene derivative  $(^{Me}[P_2Cp]Zr(\eta^2-CH_2=CH_2)Br$ (2b)directly from  $^{Me}[P_2Cp]ZrCl_3$  (1b).



Although zirconium–alkene complexes are proposed as intermediates in several important synthetic transformations, (12, 13) the number of characterizable species has been restricted to a few metallocene-type systems, (14–17) the majority of which are isolated by the use of a trapping donor (typically a phosphine) to stabilize these complexes. The ethylene derivatives introduced in this report expand this sample to include 16-electron mono(cyclopentadienyl) complexes and a related 18-electron metallocene analogue; in addition, some substitution studies are included.

#### Preparation of <sup>R</sup>[P<sub>2</sub>Cp]Zr( $\eta^2$ -CH<sub>2</sub>=CH<sub>2</sub>)Br (R = Pr<sup>*i*</sup>, Me)

A toluene solution of the starting Zr(IV) trichloride 1 reacts with 2 equiv of EtMgBr at  $-78^{\circ}$ C to give a bright yellow solution, which upon warming to room temperature produces the ethylene complex <sup>R</sup>[P<sub>2</sub>Cp]Zr( $\eta^2$ -CH<sub>2</sub>=CH<sub>2</sub>)Br (**2a**: R = Pr<sup>i</sup>; **2b**: R = Me) in excellent yield, either as dark purple (**2a**) or dark red (**2b**) crystals (Scheme 1). The yellow precursor is presumed to be the diethyl species <sup>R</sup>[P<sub>2</sub>Cp]ZrBr(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>, although no direct proof of its existence was obtained. The putative reaction sequence is completed by a  $\beta$ -H abstraction reaction with the elimination of ethane to generate the ethylene product. A quantitative halide exchange incorporates a bromide ligand in the final product, based on elemental analyses and an X-ray structural determination for **2b** (see below).

The <sup>1</sup>H and <sup>31</sup>P NMR spectra of purple **2a** are nearly identical to that of the crystallographically characterized chloro derivative <sup>Pr</sup>[P<sub>2</sub>Cp]Zr( $\eta^2$ -CH<sub>2</sub>=CH<sub>2</sub>)Cl (**2c**), a red product formed from the reaction of either alkylidene complex <sup>Pr</sup>[P<sub>2</sub>Cp]Zr=CHR(Cl) (R = Ph, SiMe<sub>3</sub>) with ethylene (18). As with **2c**, the NMR spectra for **2a** show the presence of two species in a 9:1 ratio assigned as *syn* (major) and *anti* (minor) isomers, designated according to the orientation of the ethylene ligand as being directed either *syn* or *anti* with reScheme 1.



spect to the unique carbon of the cyclopentadienyl (Cp) ring, as shown below (eq. [1]). Each isomer of 2a displays a separate singlet in the <sup>31</sup>P NMR spectrum and corresponding resonances in the <sup>1</sup>H NMR spectrum.



The ethylene protons give rise to a complex multiplet centred near 1.0 ppm in the <sup>1</sup>H NMR spectrum, originating from an AA'BB'XX' spin system due to additional  ${}^{3}J_{PH}$  coupling from the side-arm phosphines. The upfield location of these resonances in the <sup>1</sup>H NMR spectrum is indicative of an ethylene fragment coordinated to Zr. As with **2c**, definitive assignment of stereochemistry was unfortunately not possible (via <sup>1</sup>H NMR NOEDIFF experiments, for example) and so our designation of *syn* or *anti* is presumed.

In contrast to 2a, only a single species is seen in solution for the  $^{Me}[P_2Cp]$  derivative **2b**; we speculate that the reduced steric hindrance from the smaller methyl substituents at phosphorus reduces the tendency for phosphine dissociation which in turn discourages a syn/anti exchange process in this complex. The solid-state molecular structure of 2b is shown in Fig. 1, along with the atom numbering scheme. A summary of the crystallographic data is given in Table 1; selected bond distances and bond angles are listed in Table 2. The structure reveals that the ethylene unit is coordinated parallel to the Cp ring and oriented syn to the unique Cp carbon atom C(2), precisely as found for the solid state structure for 2c (18). Presumably, this orientation reduces steric interactions between the bound ethylene molecule and the Cp ring; moreover, it situates the ethylene  $\pi^*$ -orbital to overlap favorably with the filled metal  $d_{xy}$  orbital (in this

Table 1. Crystallographic data.

Compound	$\mathbf{2b}^{a}$	$syn-7a^b$
Formula	C <sub>25</sub> H <sub>51</sub> ClP <sub>2</sub> Si <sub>2</sub> Zr	C <sub>31</sub> H <sub>53</sub> ClOP <sub>2</sub> Si <sub>2</sub> Zr
Fw	596.48	686.55
Crystal system	Triclinic	Monoclinic
Space group	P-1 (no. 2)	$P2_1/c$ (no. 14)
a (Å)	15.432(3)	8.666(1)
<i>b</i> (Å)	20.483(3)	24.244(1)
<i>c</i> (Å)	20.995(7)	17.543(1)
$\alpha$ (deg)	76.50(3)	90
$\beta$ (deg)	83.12(7)	100.936(8)
γ (deg)	88.52(4)	90
V (Å <sup>3</sup> )	6407(3)	3618.9(6)
Ζ	8	4
$D_{\rm calc}$ (g cm <sup>-3</sup> )	1.24	1.260
<i>F</i> (000)	2528	1448
$\mu (cm^{-1})$	6.0	5.53
Crystal size (mm)	$0.30 \times 0.40 \times$	0.25 $ imes$ $0.35$ $ imes$
	0.45	0.45
Transmission factors	0.903-1.00	0.96-1.00
Scan type	ω-2θ	ω-2θ
Scan range (deg in $\omega$ )		$0.79 + 0.35 \tan \theta$
Scan speed (deg min <sup>-1</sup> )		16 (up to 9 scans)
Data collected	$\pm h$ , $\pm k$ , $\pm l$	
$2\theta_{\text{max}}$ (deg)	40	60
Crystal decay (%)		2.0
Total reflections	11 928	11 425
Unique reflections	11 917	10 783
R <sub>merge</sub>	0.023	0.036
No. with $I \ge 3\sigma(I)$	7589	5598
No. of variables		344
$R (F) (I \ge 3\sigma(I))$	0.055	0.034
$R_w(F)$ $(I \ge 3\sigma(I))$	0.060	0.031
$R$ ( $F^2$ ) (all data)	0.055	
$R_w$ ( $F^2$ ) (all data)	0.060	
Gof	3.71	1.49
Max $\Delta/\sigma$ (final cycle)	0.000	0.003
Residual density (e $\tilde{A}^{-3}$ )	-0.550 to 0.640	-0.35 to 0.31

<sup>a</sup>Temperature 294 K, Nonius CAD-4 diffractometer, Mo K<sub>\alpha</sub> radiation (\lambda = 0.70930 Å), graphite monochromator, takeoff angle 6.0°, aperture 6.0 × 6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan:background time ratio, 2:1),  $\sigma^2(F^2) = [S^2(C + 4B)]/Lp^2$  (S = scan rate, C = scan count, B = normalized background count), function minimized  $\Sigma w(|F_o| - |F_c|)^2$  where  $w = 4F_o^2/\sigma^2(F_o^2)$ , R (F) =  $\Sigma ||F_o| - |F_c||/\Sigma |F_o|$ ,  $R_w$  (F) =  $(\Sigma w(|F_o| - |F_c|)^2/(m - n))^{1/2}$ .

<sup>b</sup>Temperature 294 K, Rigaku AFC6S diffractometer, Mo K<sub>\alpha</sub> radiation ( $\lambda = 0.71069$  Å), graphite monochromator, takeoff angle 6.0°, aperture 6.0 × 6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan:background time ratio, 2:1),  $\sigma^2(F^2) = [S^2(C + 4B)]/Lp^2$  (S = scan rate, C = scan count, B = normalized background count), function minimized  $\Sigma w(|F_0| - |F_c|)^2$  where  $w = 4F_o^2/\sigma^2(F_o^2)$ , R ( $F) = \Sigma ||F_0| - |F_c||/\Sigma |F_0|$ ,  $R_w$  ( $F) = (\Sigma w(|F_0| - |F_c|)^2/(m - n)]^{1/2}$ .

representation the *z*-axis passes through the Cp-centroid). Previous investigations into bonding interactions in electronrich complexes with piano-stool geometries suggest that the metal  $d_{xy}$  orbital offers the best electron donation to a  $\pi$ -acceptor ligand (19, 20). The C(16)—C(17) bond distance of 1.431(6) Å in **2b** is comparable to the corresponding value of 1.433(17) Å for **2c**, which illustrates that the degree of **Fig. 1** Molecular structure of  ${}^{Me}[P_2Cp]Zr(\eta^2-CH_2=CH_2)Br$  (**2b**); 33% probability thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity.



**Table 2.** Selected bond lengths (Å) and bond angles (°) for  $^{Me}[P_2Cp]Zr(\eta^2-CH_2=CH_2)Br$  (**2b**).

Bond lengths (Å)		Bond angles (°)	
$\overline{\text{Zr}(1)}$ — $\text{Br}(1)$	2.6744(6)	Br(1)-Zr(1)-P(1)	78.28(3)
Zr(1) - P(1)	2.730(1)	Br(1)- $Zr(1)$ - $P(2)$	76.94(3)
Zr(1) - P(2)	2.703(1)	Br(1)-Zr(1)-C(16)	109.7(1)
Zr(1)—C(16)	2.293(5)	Br(1)-Zr(1)-C(17)	109.7(1)
Zr(1) - C(17)	2.312(5)	P(1)- $Zr(1)$ - $P(2)$	155.17(4)
Zr(1)— $Cp'$	2.23	P(1)-Zr(1)-C(16)	75.6(1)
C(16)—C(17)	1.431(6)	P(1)-Zr(1)-C(17)	111.0(1)
		C(16)-Zr(1)-C(17)	36.2(2)

backbonding is not significantly altered upon substituting either the halide (Br for Cl) or the groups attached to the phosphines (methyl for isopropyl). However, the phosphines are bound considerably closer to the metal in **2b**, with Zr—P bond distances averaging 2.72 Å in comparison to 2.86 Å for **2c**. The C—C bond distance of the ethylene ligand is similar in these complexes to that found for other monomeric Zr(II) ethylene complexes (14, 16, 21). The lengthening of this bond compared to 1.337 Å found in free ethylene (22) is indicative of significant back-bonding from the metal as represented in the Dewar–Chatt–Duncanson model (23, 24) and supports a Zr(IV) metallacyclopropane bonding depiction (**A**). Also consistent with this formalism are the short Zr—C bond lengths (average 2.30 Å) in **2b**, which are within the range of typical Zr—C single bonds (12) and considerably shorter than the Zr—C distance of 2.68 (2) in a cationic Zr(IV) olefin complex in which  $d-\pi^*$  back-bonding is unavailable (25).



By NMR spectroscopy, only one isomer is seen for 2b in solution, thus it is assumed that it corresponds to the *syn* structure observed in the solid state. The similarities between the <sup>1</sup>H NMR spectrum of the major isomer of 2a with that of the single species seen for 2b, particularly in the distinctive Cp region, suggests that the major isomer of 2a is the *syn* isomer as well.

The formation of the ethylene complexes 2a and 2b directly from the respective starting trichlorides offers a facile alternative to the multistep approach to 2c (i.e., via an alkylidene complex) (18). This general synthetic route has been employed elsewhere to obtain a number of early metal alkene complexes (15). Unfortunately, this procedure could not be extended to other Zr alkene complexes with this system. For example, propylene complexes could not be isolated by using Grignard reagents such as Pr<sup>n</sup>MgBr or Pr<sup>i</sup>MgCl, nor was Bu<sup>n</sup>Li effective in obtaining a coordinated butene species. All of these attempts resulted in complete consumption of the starting materials, but no isolable alkene complexes were forthcoming; this is reminiscent of the reactions of substituted alkenes with the related alkylidene complexes (18). The apparent instability of these complexes incorporating higher alkenes may be due to a combination of greater steric hindrance from the bulky ancillary ligand along with weaker bonding of these alkenes relative to ethylene.

# Preparation of $\Pr[P_2Cp]Zr(\eta^2-CH_2=CH_2)R'$ (R' = Me, C<sub>5</sub>H<sub>5</sub>)

In an attempt to expand the scope of ethylene complexes for which reactivity studies could be compared, we examined the preparation of alkyl-ethylene derivatives by standard metathesis reactions involving the bromide ligand (Scheme 2).

The characteristic spectroscopic feature of the methyl derivative **3a** is the triplet  $({}^{3}J_{PH} = 10 \text{ Hz})$  at -0.67 ppm in the  ${}^{1}\text{H}$  NMR spectrum for the methyl group attached to Zr. The distinctive Cp region of this spectrum is nearly identical to that of the major *syn* isomer of **2**, suggesting that the solution structure of **3a** (only one species is seen) is exclusively the *syn* isomer. Unfortunately this complex was only characterized in solution as it could not be isolated as a solid, despite many attempts; decomposition with the elimination of ethylene to give unidentified products was observed.

The Cp derivative **4a** could be isolated as reddish-orange crystals. There are two equal intensity singlets in the  $^{31}$ P NMR spectrum for **4a** at -5.3 ppm and 42.3 ppm; the peak

Scheme 2.



at -5.3 ppm for this ligand system is indicative of an uncoordinated phosphine, while the other resonance at 42.3 corresponds to a bound phosphine donor. The <sup>1</sup>H NMR spectrum shows a doublet ( ${}^{3}J_{PH} = 2$  Hz) at 5.20 ppm for the five protons of the C<sub>5</sub>H<sub>5</sub> ring; the downfield chemical shift suggests that this ligand is coordinated in an  $\eta^{5}$ -mode. As the array of ligands in this complex is similar to that found in the structurally characterized metallocene derivative Cp<sub>2</sub>Zr( $\eta^{2}$ -CH<sub>2</sub>=CH<sub>2</sub>)(PMe<sub>3</sub>), (14, 21) it is reasonable to consider an analogous structure for **4a** as shown below.



The asymmetric geometry renders all four ethylene protons inequivalent, thus generating a complicated second order splitting pattern in the <sup>1</sup>H NMR spectrum (with additional coupling to the coordinated phosphine). This asymmetry is also evident from the three separate resonances observed for the cyclopentadienyl portion of the P<sub>2</sub>Cp ancillary ligand. The presence of only one coordinated phosphine in **4a** supports the view of the C<sub>5</sub>H<sub>5</sub> ligand as  $\eta^5$ bound; the steric and electronic saturation provided by this coordination mode yields an 18-electron species which would force one side-arm to remain dangling, as observed. The ethylene unit and the coordinated phosphine thus can be considered to be occupying the metallocene wedge, with the other side-arm left out of the coordination sphere.

#### Ligand substitution reactions with CO

A purple toluene solution of the ethylene complex 2a reacts instantly under an atmosphere of CO to generate a dark greenish-orange solution that shows a single resonance in the <sup>31</sup>P NMR spectrum at 29.1 ppm. In the <sup>1</sup>H NMR spectrum the only resonances observed are attributed to the ancillary ligand, and a sealed NMR tube reaction reveals a singlet at 5.25 ppm for the evolution of free ethylene. A similar result is obtained in the reaction with **2b**. Therefore, it is apparent in both instances that the coordinated ethylene unit has been replaced by CO in a ligand substitution reaction to give a carbonyl complex (eq. [2]).



For the reaction of 2a with <sup>13</sup>CO the downfield region of the <sup>13</sup>C NMR spectrum displays two carbonyl peaks at 241 and 249 ppm for 5a in addition to a third resonance at 184 ppm for excess free <sup>13</sup>CO, indicating that an 18-electron dicarbonyl species has been formed from the 16-electron precursor. In 5b the carbonyl resonances are located at 240 and 245 ppm, respectively. These complexes have a ligand arrangement that is similar to known derivatives such as CpZr(CO)<sub>2</sub>(dmpe)Cl (26). The presence of a carbonyl ligand is supported by absorptions in the IR spectra at 1890 and 1898 cm<sup>-1</sup> for **5a** and **5b**, respectively, which shift to 1865 and 1855 cm<sup>-1</sup> for the <sup>13</sup>C labeled isotopomers. The low  $v_{CO}$ values of the coordinated carbonyl ligands in comparison to free CO ( $v_{CO} = 2143 \text{ cm}^{-1}$ ) are due to strong back-bonding from the electron-rich Zr(II) centre to the  $\pi^*$  orbital of the CO ligand and is consistent with the stretching frequency in analogous Zr(II) carbonyls (i.e.,  $CpZr(CO)_2(dmpe)Cl$ ,  $v_{CO} =$ 1940 cm<sup>-1</sup>) (26). Unfortunately, although both carbonyl complexes 5a and 5b are stable indefinitely in solution in the presence of excess CO, attempts to isolate these species in the absence of CO led to decomposition. This instability outside of a protective CO atmosphere has been noted with other Zr carbonyl derivatives (26-28), demonstrating the labile nature of these ligands with early metals.

A notable feature of the ambient temperature  ${}^{13}$ C NMR spectrum of **5a** is that the peak for free CO at 184 ppm is broadened, as is the carbonyl peak at 241 ppm. This obser-

Fig. 2 Variable temperature  ${}^{13}$ C NMR spectra of  ${}^{Pr}[P_2Cp]Zr(CO)_2Br$  (5a).



vation suggests that this CO ligand is undergoing an exchange process with free CO in solution; the remaining ligand is either not involved in this process or is at the slow exchange limit at this temperature, since the peak for this ligand at 249 ppm is quite sharp in comparison. This exchange process was monitored by variable temperature <sup>13</sup>C NMR spectroscopy and a selection of the spectra are shown in Fig. 2; these spectra demonstrate an increase in line broadening as the temperature is raised, in agreement with an increase in the exchange rate between free CO and the exchanging carbonyl ligand.

The NMR spectra were simulated (using DNMR-5)<sup>®</sup> to obtain rate constants at each temperature, which were used in the resulting Eyring plot shown in Fig. 3. The kinetic parameters  $\Delta H^{\ddagger} = 9.2(5)$  kcal mol<sup>-1</sup> and  $\Delta S^{\ddagger} = -17(2)$  cal mol<sup>-1</sup> K<sup>-1</sup> were calculated from this plot. The negative entropy term is unexpected, as ligand exchange from this saturated 18-electron species is anticipated to proceed in a dissociative mechanism that should produce a positive entropy term for a less ordered transition state. A concerted mechanism involving dissociation of a pendant phosphine may therefore be a factor in this exchange. An associative process has also been suggested from a separate kinetic study into similar CO ligand exchange in other 18-electron Zr carbonyl species (27, 28).

Ligand exchange is common for early metal carbonyl complexes. In the related complex  $Cp*Hf(CO)_2(dmpe)Cl$  (28) both CO ligands are observed to rapidly and quantitatively exchange with excess <sup>13</sup>CO. One can speculate as to

Fig. 3 Eyring plot for the CO ligand exchange process in  $\Pr[P_2Cp]Zr(CO)_2Br$  (5a).



#### why only one carbonyl ligand in 5a undergoes this exchange. If we assume that the quasioctahedral geometry shown in eq. [2] holds here, then for such mono(cyclopentadienyl) type complexes the ligand located trans to the Cp donor is typically weakly bound, (29) with labile coordination observed in some instances (30). Thus for 5a, it is the carbonyl ligand located at this labile site that undergoes exchange while the other trans to the bromide remains unaffected. To rationalize this observation, one can invoke two complementary effects: first, the strong labilizing trans effect of the Cp donor contrasts with the weak trans effect of the electron withdrawing bromide, and second, and as noted for 2b, backbonding from the zirconium in monocyclopentadienyl complexes is optimized by the $d_{xy}$ orbital (and to a lesser extent the $d_2$ orbital), which is well suited to stabilize the carbonyl trans to the bromide but of negligible use for

The reactivity of the 18-electron ethylene complex **4a** with CO was examined to compare with the results observed for the 16-electron analogue **2a**. As opposed to **2a**, which coordinates CO almost instantly, the reaction of **4a** with CO is considerably slower, requiring more than two weeks for completion under the same reaction conditions (eq. [3]). This remarkable difference in reaction times can be traced to the electronic saturation in **4a**, adding further evidence that the  $C_5H_5$  donor in this complex is  $\eta^5$ -coordinated. As a result, in lieu of a 20-electron intermediate in this reaction, either a ligand must dissociate or alternatively the Cp ring must undergo  $\eta^5$ - $\eta^3$  ring slippage, prior to the coordination of a CO molecule.

the other carbonyl ligand *trans* to the Cp group.



The eventual product from the above reaction is the carbonyl species  ${}^{Pr}[P_2Cp]Zr(CO)(\eta {}^5-C_5H_5)$  (6a), which is ac-

companied by the evolution of free ethylene as observed with the analogous reaction that forms carbonyl **5**. The <sup>31</sup>P NMR spectrum of **6a** is similar to that of the precursor **4a**, with one singlet at 58.7 ppm and another at –4.8 ppm. In the <sup>1</sup>H NMR spectrum only resonances attributed to the ancillary ligand and the Cp ligand are evident. The presence of the carbonyl ligand is indicated in the <sup>13</sup>C NMR spectrum by a single downfield resonance at 308 ppm (<sup>2</sup>J<sub>PC</sub> = 2 Hz) in the reaction of **4a** with <sup>13</sup>CO. As an analogue of the 18electron metallocene carbonyl species Cp<sub>2</sub>Zr(CO)(PMe<sub>3</sub>) (31), the proposed structure of **6a** is depicted as shown below.



In contrast to **5a**, the line width of the carbonyl peak for **6a** is very narrow, with no evidence for exchange with the narrow peak at 184 ppm due to excess <sup>13</sup>CO. The difference in the respective lability of the carbonyl ligands in **5a** vs. **6a** may originate from the presence of one less CO ligand in **6a**, which is not in competition for backbonding and hence is less labile. The contrasting rapid CO exchange observed for the similar metallocene analogue  $Cp_2Zr(CO)_2$  (27) is in accord with this view, where two carbonyl ligands are in competition for backbonding from the same filled donor orbital (32).

# Preparation of <sup>Pr</sup>[P<sub>2</sub>Cp]Zr(η<sup>2</sup>-PhCCPh)Br

Given the facile ligand substitution reaction observed for the ethylene derivatives 2a and 2b with CO, and the observed tendency for early metal alkene complexes to undergo substitution reactions with alkynes, (33, 34) the reaction with diphenylacetylene was examined with this system. A toluene solution of ethylene 2a reacts with 1 equiv of diphenylacetylene (PhCCPh) under ambient conditions to displace the ethylene ligand and generate the alkyne complex  $\Pr[P_2Cp]Zr(\eta^2-PhCCPh)Br$  (7a), which can be isolated as pale yellow crystals (Scheme 3). In contrast to the immediate displacement of ethylene by CO to give carbonyl 5a, the corresponding ligand substitution reaction of 2a with diphenylacetylene is slower, requiring 24 h for completion. This observation is consistent with steric factors inducing a slower rate for the bulky alkyne in comparison to the small linear CO molecule, and points to a probable requirement that a phosphine must dissociate to allow room for the incoming alkyne.

In solution alkyne **7a** exists as two isomers in a 3:2 ratio, based on the <sup>1</sup>H and <sup>31</sup>P NMR spectra. There are two singlets in the <sup>31</sup>P NMR spectrum, one each for the major (8.5 ppm) and minor isomer (11.6 ppm), respectively, and a

Scheme 3.



**Table 3.** Selected bond lengths (Å) and bond angles (°) for  $\Pr[P_2Cp]Zr(\eta^2-PhCCPh)Br$  (*syn-7a*).

Bond lengths (Å)		Bond angles (°)	
$\overline{\text{Zr}(1)}$ —Br(1)	2.6771(5)	Br(1)-Zr(1)-P(1)	78.61(2)
Zr(1) - P(1)	2.8367(8)	Br(1)-Zr(1)-P(2)	76.35(2)
Zr(1) - P(2)	2.8129(8)	Br(1)-Zr(1)-C(24)	102.85(8)
Zr(1)—C(24)	2.197(3)	Br(1)-Zr(1)-C(25)	116.88(8)
Zr(1)—C(25)	2.182(2)	P(1)-Zr(1)-P(2)	154.87(4)
Zr(1)— $Cp'$	2.264	P(1)-Zr(1)-C(24)	77.57(7)
C(24)—C(25)	1.322(6)	Zr(1)-C(24)-C(26)	111.0(1)
C(24)—C(26)	1.471(4)	C(25)-C(24)-C(26)	126.8(2)

corresponding set of resonances in the <sup>1</sup>H NMR spectrum for each species. As found with other complexes having this ancillary ligand system (18) and observed for 2a, the two species seen for 7a are likely the syn and anti stereoisomers. A variable temperature NMR study indicates that these isomers interconvert, as evidenced by increased line broadening in both peaks in the <sup>31</sup>P NMR spectrum as the temperature is raised. Curiously, a change in the equilibrium ratio of these species was not detected from this experiment. A <sup>1</sup>H NOEDIFF NMR experiment was performed, from which it was determined that the anti isomer is the major species in solution. Irradiation of the resonance assigned to the two equivalent protons in the Cp ring of the major isomer showed an enhancement of the signals for the ortho protons of the phenyl ring; no effect was detected when the unique Cp proton resonance was irradiated.

The molecular structure of alkyne **7a** was determined by an X-ray crystal structure analysis and is shown in Fig. 4. Selected bond lengths and bond angles are listed in Table 3. The solid-state structure corresponds to the minor *syn* isomer, with the alkyne coordinated parallel to the Cp ring as found for the ethylene ligand in **2b**. However, in *syn*-**7a** the alkyne unit is tilted from this parallel orientation by approximately 9°. The short Zr(1)—C(24) and Zr(1)—C(25) bond lengths of 2.20 Å and 2.18 Å, respectively, are indicative of strong back-bonding from the metal. This is also reflected in the C(25)-C(24)-C(26) bond angle of 127° that illustrates the **Fig. 4** Molecular structure of  $\Pr[P_2Cp]Zr(\eta^2-PhCCPh)Br$  (*syn-7a*); 33% probability thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity.



degree to which the phenyl rings are pulled back from the metal as a result of this back-donation. This geometry of the coordinated alkyne resembles that of a metallacyclopropene **C**, rather than a simple  $\pi$ -bound alkyne as shown in **D** (6). The double bond character of the coordinated alkyne is indicated by the C(24)—C(25) bond distance of 1.322(6) Å. These structural parameters are similar to those of the structurally characterized Zr alkyne complex Cp<sub>2</sub>Zr( $\eta^2$ -PhCCPh)(PMe<sub>3</sub>) (34).



A comparison of the bonding in *syn*-7a with that of the ethylene complex 2b shows in each case that back-bonding from the metal induces lengthening of the coordinated C—C bond (compared to the free substrate). In addition, alkynes have a second  $\pi$ -orbital that can overlap with a metal *d* orbital of suitable symmetry to form a  $\pi$ -bond, such that this ligand can potentially be represented as a four-electron donor. However, in 7a this interaction is in competition with one of the  $\pi$ -donor orbitals from the Cp ring, which diminishes the ability of the alkyne to donate electron density from this second  $\pi$ -orbital. But the observation that alkyne

**7a** is unreactive in the presence of CO is in direct contrast to the rapid reaction seen for ethylene **2a**, which otherwise has the same ligand coordination sphere. Assuming that steric considerations are minimal for a small nucleophile such as CO, this difference in reaction times suggests that the alkyne complex **7a** is a fully saturated 18-electron species, implying that there is at least some component present to the additional  $\pi$ -bond from the alkyne to the metal centre.

#### **Experimental section**

#### **General considerations**

Unless otherwise stated all manipulations were performed under an atmosphere of prepurified nitrogen in a Vacuum Atmospheres HE-553-2 glove box equipped with a MO-40-2H purification system or in standard Schlenk-type glassware on a dual vacuum-nitrogen line. Reactions involving gaseous reagents were conducted in Pyrex vessels (bombs) designed to withstand pressures up to 10 atm (1 atm = 101.325 kPa). <sup>1</sup>H NMR spectra (referenced to either  $C_6D_5H$ or  $C_6D_5CD_2H$  for benzene and toluene, respectively) were performed on one of the following instruments depending on the complexity of the particular spectrum: Bruker WH-200, Varian XL-300, or a Bruker AM-500. <sup>13</sup>C NMR spectra (referenced to solvent peaks) were run at 50.323 MHz on the Bruker WH-200 or at 75.429 MHz on the XL-300 instrument, and <sup>31</sup>P NMR spectra (referenced to external P(OMe)<sub>3</sub> at 141.0 ppm) were run at 121.421 MHz and 202.33 MHz, on the XL-300 and Bruker AM-500 instruments, respectively. All chemical shifts are reported in ppm and all coupling constants are reported in Hz. Infrared spectra were recorded on a BOMEM MB-100 spectrometer. Solution samples were recorded on a 0.1 mm KBr cell and solid samples were recorded as pellets. Elemental analyses (Mr. P. Borda) and GC-MS were performed within this department.

#### Reagents

Ethylene and carbon monoxide were obtained as lecture bottles from Matheson and dried over P2O5 before use. Labeled <sup>13</sup>CO (Cambridge Isotopes) was used as received. Diphenylacetylene (Aldrich) was sublimed before use. MeMgBr (1.4 M solution in THF-toluene) and EtMgBr (3.0 M solution in ether) were purchased from Aldrich and used as received. NaCp(DME) (DME = dimethoxyethane) was prepared according to published literature procedure (35). Hexanes, tetrahydrofuran (THF), and toluene were predried over CaH<sub>2</sub> followed by distillation under argon from either sodium metal or sodium-benzophenone ketyl; pentane was distilled from sodium-benzophenone ketyl. The deuterated solvents C<sub>6</sub>D<sub>6</sub> and C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub> were dried over sodium, vacuum transferred to a bomb, and degassed by freeze-pump-haw technique before use. The procedures for the preparation of  ${}^{R}[P_{2}Cp]ZrCl_{3}$  (1a: R = Pr<sup>*i*</sup> (36); 1b: R = Me<sup>3</sup>) have been described elsewhere.

#### $Pr[P_2Cp]Zr(\eta^2-CH_2=CH_2)Br$ (2a)

A solution of 3.0 M EtMgBr (2.15 mL, 6.45 mmol) was diluted in 20 mL of toluene and added dropwise with stirring to a cooled ( $-78^{\circ}$ C) solution of **1a** (2.06 g, 3.23 mmol) dissolved in 100 mL of toluene. The pale yellow colour of

the solution turned to bright yellow upon addition. The mixture was stirred at  $-78^{\circ}$ C for 1 h and allowed to slowly warm to room temperature, whereupon the colour of the solution gradually changed to a dark reddish purple. The volatiles were then removed under vacuum and the residue extracted with pentane and filtered. Dark purple crystals of **2a** were obtained from a cold ( $-40^{\circ}$ C) concentrated pentane solution. Yield: 1.86 g (90%). <sup>1</sup>H NMR (20°C, C<sub>6</sub>D<sub>6</sub>)  $\delta$ : 0.21 and 0.23 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.82 and 0.85 (d, 2H, <sup>2</sup>J<sub>PH</sub> = 8 Hz, SiCH<sub>2</sub>P), 0.98 and 1.01 (m, 2H, <sup>3</sup>J<sub>PH</sub> = 7 Hz, CH<sub>2</sub>=CH<sub>2</sub>), 1.08, 1.15, 1.26, and 1.31 (dd, 6H, <sup>2</sup>J<sub>HH</sub> = 7 Hz, <sup>2</sup>J<sub>PH</sub> = 7 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 2.23 and 2.35 (sept, 2H, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 4.37 (t, 1H, <sup>4</sup>J<sub>HH</sub> = 1 Hz, Cp-H), 6.31 (d, 2H, <sup>4</sup>J<sub>HH</sub> = 2 Hz, Cp-H). <sup>31</sup>P NMR (20°C, C<sub>6</sub>D<sub>6</sub>)  $\delta$ : 19.5 (s). Anal. calcd. for C<sub>25</sub>H<sub>51</sub>BrP<sub>2</sub>Si<sub>2</sub>Zr: C 46.85, H 8.02; found: C 46.89, H 8.06.

## $^{Me}[P_2Cp]Zr(\eta^2-CH_2=CH_2)Br(2b)$

A solution of 3.0 M EtMgBr (1.50 mL, 4.50 mmol) was diluted in 20 mL of toluene and added dropwise with stirring to a cooled ( $-78^{\circ}$ C) solution of **1b** (1.19 g, 2.26 mmol) dissolved in 40 mL of toluene. The reaction mixture was allowed to warm to room temperature and stirred for 3 h, during which a dark reddish brown colour was generated. The solvent was removed and the residue extracted with hexanes and filtered. Reducing this solution to 5 mL permitted the isolation of dark red crystals at  $-40^{\circ}$ C, which were washed with cold pentane and dried. Yield: 0.93 g (79%). <sup>1</sup>H NMR (20°C, C<sub>6</sub>D<sub>6</sub>) & 0.09 and 0.16 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.84 and 1.15 (d, 2H, <sup>2</sup>*J*<sub>HH</sub> = 12 Hz, SiCH<sub>2</sub>P), 0.88 and 1.33 (d, 2H, <sup>3</sup>*J*<sub>PH</sub> = 9 Hz, CH<sub>2</sub>=CH<sub>2</sub>), 1.24 and 1.27 (d, 6H, <sup>2</sup>*J*<sub>PH</sub> = 7 Hz, P(CH<sub>3</sub>)<sub>2</sub>), 4.15 (t, 1H, <sup>4</sup>*J*<sub>HH</sub> = 1 Hz, Cp-*H*), 6.02 (d, 2H, <sup>4</sup>*J*<sub>HH</sub> = 1 Hz, Cp-*H*). <sup>31</sup>P NMR (20°C, C<sub>6</sub>D<sub>6</sub>) & 0.0 (s). Anal. calcd. for C<sub>17</sub>H<sub>35</sub>BrP<sub>2</sub>Si<sub>2</sub>Zr: C 38.62, H 6.67; found: C 38.54, H 6.74.

#### $P^{r}[P_{2}Cp]Zr(\eta^{2}-CH_{2}=CH_{2})Me$ (3a)

A solution of 1.4 M MeMgBr (0.75 mL, 1.05 mmol) was diluted in 10 mL of toluene and added dropwise with stirring to a cooled ( $-78^{\circ}$ C) solution of **2a** (620 mg, 0.97 mmol) dissolved in 30 mL of toluene. The mixture was allowed to slowly warm to room temperature, during which the colour of the solution gradually changed from a deep purple to a dark reddish orange. The reaction mixture was stirred for another 24 h, the volatiles were then removed under vacuum and the residue extracted with hexanes and filtered. An impure pale pink solid was obtained by slow evaporation of the filtrate, which gradually decomposed with the evolution of free ethylene. <sup>1</sup>H NMR (20°C, C<sub>6</sub>D<sub>6</sub>)  $\delta$ : -0.67 (t, 3H, <sup>3</sup>J<sub>PH</sub> = 10 Hz, ZrCH<sub>3</sub>), 0.24 and 0.26 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.86 (m, 4H, <sup>2</sup>J<sub>PH</sub> = 8 Hz, SiCH<sub>2</sub>P), 1.05 (m, 2H, <sup>3</sup>J<sub>PH</sub> = 8 Hz, Zr(CH<sub>2</sub>=CH<sub>2</sub>)), 1.10 (m, 24H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.09 (sept, 4H, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 4.61 (t, 1H, <sup>4</sup>J<sub>HH</sub> = 2 Hz, Cp-H), 6.32 (d, 2H, <sup>4</sup>J<sub>HH</sub> = 2 Hz, Cp-H). <sup>31</sup>P NMR (20°C, C<sub>6</sub>D<sub>6</sub>)  $\delta$ : 20.1 (s).

# $Pr[P_2Cp]Zr(\eta^2 - CH_2 = CH_2)(\eta^5 - C_5H_5)$ (4a)

A solution of NaCp(DME) (106 mg, 0.59 mmol) in 30 mL of toluene was added dropwise with stirring to a cooled ( $-78^{\circ}$ C) solution of **2a** (410 mg, 0.59 mmol) dis-

solved in 50 mL of toluene. The mixture was stirred at -78°C for 2 h, then allowed to slowly warm to room temperature and stirred for another 24 h The colour of the solution gradually changed from a deep purple to a orange-red. The volatiles were then removed under vacuum and the residue extracted with hexanes and filtered. Orange crystals were obtained from a cold (-40°C) concentrated hexamethyldisiloxane-hexanes mixture. The crystals were washed with cold hexamethyldisiloxane and dried. Yield: 310 mg (84%). <sup>1</sup>H NMR (20°C,  $C_6D_6$ )  $\delta$ : 0.08, 0.13, 0.52 and 0.58 (s, 3H,  $Si(CH_3)_2$ , 0.42, 0.75, and 0.85 (ddt, 1H,  ${}^3J_{HH} = 10$  Hz (*cis* and *trans*),  ${}^{3}J_{PH} = 6$  Hz, CH*H*=CH<sub>2</sub>), 0.74 and 0.81 (dd, 2H,  ${}^{2}J_{HH} = 15$  Hz,  ${}^{2}J_{PH} = 4$  Hz, SiCH<sub>2</sub>P), 0.94, 1.00, 1.02, 1.03, 1.04, 1.05, 1.05, and 1.13 (dd, 3H,  ${}^{3}J_{HH} = 7$  Hz,  ${}^{3}J_{PH} = 7$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.59 and 1.60 (sept, 1H,  ${}^{3}J_{HH} = 7$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.59 and 1.60 (sept, 1H,  ${}^{3}J_{HH} = 7$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.74 (d of sept, 1H,  ${}^{3}J_{HH} = 7$  Hz,  ${}^{2}J_{PH} = 3$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.98 (d of sept, 1H,  ${}^{3}J_{HH} = 7$  Hz,  ${}^{2}J_{PH} = 7$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 5.21 (t, 1H,  ${}^{4}J_{HH} = 2$  Hz, Cp-H), 5.35, (s, 5H,  ${}^{3}J_{PH} = 1$  Hz, C<sub>5</sub>H<sub>5</sub>), 5.61 and 5.62 (dd, 1H,  ${}^{3}J_{HH} = 6$  Hz,  ${}^{4}J_{HH} = 2$  Hz, Cp-H).  ${}^{31}P$  NMR (20°C, C<sub>6</sub>D<sub>6</sub>) & -5.3 (s), 42.3 (s). Anal. calcd. for  $C_{30}H_{56}P_2Si_2Zr$ : C 57.55, H 9.01; found: С 57.25, Н 9.15.

#### $Pr[P_2Cp]Zr(CO)_2Br$ (5a)

A benzene- $d_6$  solution of **2a** was placed in a sealable NMR tube and affixed to a dual vacuum-nitrogen line. A small portion of solvent was removed under vacuum, and an atmosphere of carbon monoxide introduced at -78°C. The colour of the solution instantly changed from dark purple to dark green. <sup>1</sup>H NMR spectroscopy revealed the evolution of free ethylene and the formation of one clean product with resonances associated solely with the ancillary ligand, while the <sup>31</sup>P NMR spectrum showed a single new resonance. Repeating the reaction in a sealed tube with the addition of <sup>13</sup>CO yielded diagnostic peaks for the carbonyl ligands in the <sup>13</sup>C NMR spectrum. Conducting the reaction on a larger scale in toluene generated the same colour change in solution as noted before upon addition of CO, although removal of the volatiles induced a subtle degradation of the green colour to this solution. A hydrocarbon-soluble, thermally labile dark orange-green oil was obtained after workup in hexanes. IR  $(C_6D_6)$   $v_{CO}$  (cm<sup>-1</sup>): 1890, 1865 (<sup>13</sup>CO). <sup>1</sup>H NMR  $(20^{\circ}\text{C}, \text{ C}_6\text{D}_6)$  & 0.12 and 0.28 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.51 and 0.82 (dd, 2H,  ${}^{2}J_{HH} = 15$  Hz,  ${}^{2}J_{PH} = 9$  Hz, SiCH<sub>2</sub>P), 0.97, 1.22, 1.29 and 1.32 (dd, 6H,  ${}^{3}J_{HH} = 7$  Hz,  ${}^{3}J_{PH} = 7$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.95 and 2.48 (sept, 2H,  ${}^{3}J_{HH} = 7$  Hz,  $CH(CH_3)_2$ ), 5.16 (d, 2H,  ${}^4J_{HH} = 1$  Hz, Cp-H), 5.19 (t, 1H,  ${}^4J_{HH} = 1$  Hz, Cp-H).  ${}^{13}C$  NMR (20°C, C<sub>6</sub>D<sub>6</sub>) & 241.1 (br s, Zr(CO)), 249.1 (s, Zr(CO)). <sup>31</sup>P NMR (20°C, C<sub>6</sub>D<sub>6</sub>) δ: 29.1 (s).

#### $^{Me}[P_2Cp]Zr(CO)_2Br$ (5b)

The procedure followed was similar to that for **5a**, reacting ethylene **2b** in an atmosphere of CO. The colour of the solution gradually changed from dark red to a dull purplish red after the addition of CO. Once again, a scaled up version of this reaction permitted only the isolation of a thermally labile oil. IR ( $C_6D_6$ )  $v_{CO}$  (cm<sup>-1</sup>): 1898, 1855 ( $^{13}CO$ ) <sup>1</sup>H NMR (20°C,  $C_6D_6$ )  $\delta$ : 0.09 and 0.18 (s, 6H, Si( $CH_3$ )<sub>2</sub>), 0.57 and 1.03 (d, 2H,  $^2J_{PH} = 7$  Hz, SiCH<sub>2</sub>P), 1.41 and 1.50 (t, 6H,  $^2J_{PH} = 5$  Hz, P(CH<sub>3</sub>)<sub>2</sub>), 4.82 (d, 2H,  $^4J_{HH} = 1$  Hz, Cp-H),

5.08 (t, 1H,  ${}^{4}J_{HH} = 1$  Hz, Cp-*H*).  ${}^{13}C$  NMR (20°C, C<sub>6</sub>D<sub>6</sub>)  $\delta$ : 240.5 and 245.1 (s, Zr(*CO*)).  ${}^{31}P$  NMR (20°C, C<sub>6</sub>D<sub>6</sub>)  $\delta$ : -12.0 (s).

#### $P^{r}[P_{2}Cp]Zr(\eta^{5}-C_{5}H_{5})(CO)$ (6a)

A benzene- $d_6$  solution of **4a** was placed in a sealable NMR tube and affixed to a dual vacuum-nitrogen line. A small portion of solvent was removed under vacuum, and an atmosphere of carbon monoxide introduced at -78°C. The contents within the sample were continually mixed under ambient temperature by a constant inversion of the sample by mechanical method. The reaction was monitored by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy until the reaction was complete (approximately 2 weeks). There was no obvious colour change associated with this reaction. 6a was observed to be the major product (90%) based on the NMR spectra. Repeating the procedure in a sealed tube with the addition of <sup>13</sup>CO yielded a strong diagnostic peak at 308 ppm for the carbonyl ligand in the <sup>13</sup>C NMR spectrum. Conducting the reaction on a larger scale in toluene generated a thermally sensitive hydrocarbon-soluble orange oil after workup that gradually decomposed at  $-40^{\circ}$ C. <sup>1</sup>H NMR (20°C, C<sub>6</sub>D<sub>6</sub>)  $\delta$ : 0.13, 0.24, 0.35, and 0.47 (s, 3H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.42 and 0.63 (dd, 1H,  ${}^{2}J_{HH} = 11$  Hz,  ${}^{2}J_{PH} = 9$  Hz, SiC $H_{2}$ P), 0.69 (d, 2H,  ${}^{2}J_{PH} = 7 \text{ Hz}, \text{ Si}CH_2\text{P}, 0.75, 0.78, 0.90, and 0.91 (dd, 3H, {}^{3}J_{HH} = 7 \text{ Hz}, {}^{3}J_{PH} = 7 \text{ Hz}, CH(CH_3)_2), 1.05 (m, 12H, CH(CH_3)_2), 1.29 and 1.55 (sept, 1H, {}^{3}J_{HH} = 7 \text{ Hz}, 26 \text{ Hz}, {}^{3}J_{HH} = 7 \text{ Hz}, {}^{3}J_{H} = 7 \text{ Hz},$  $CH(CH_3)_2$ , 1.59 (sept, 2H,  ${}^{3}J_{HH} = 7$  Hz,  $CH(CH_3)_2$ ), 4.95 (s, 5H,  ${}^{3}J_{PH} = 1$  Hz, C<sub>5</sub>H<sub>5</sub>), 5.08, 5.55, and 5.62 (dd, 1H,  ${}^{4}J_{HH} = 1$  Hz, Cp-H).  ${}^{13}C$  NMR (20°C, C<sub>6</sub>D<sub>6</sub>)  $\delta$ : 308.0 (d,  ${}^{2}J_{PC} =$ 3 Hz, Zr(CO)). <sup>31</sup>P NMR (20°C,  $C_6D_6$ )  $\delta$ : -4.8 and 58.7 (s).

#### $P^{r}[P_{2}Cp]Zr(\eta^{2}-PhCCPh)Br$ (7*a*)

Diphenylacetylene (106 mg, 0.59 mmol) was dissolved in 30 mL of toluene and added dropwise with stirring to a cooled ( $-78^{\circ}$ C) solution of **2a** (410 mg, 0.59 mmol) dissolved in 50 mL of toluene. The mixture was slowly warmed to room temperature and stirred for another 24 h. The colour of the solution gradually changed from a deep purple to a dark brown. The volatiles were then removed under vacuum and the residue extracted with hexanes and filtered. Pale yellow crystals were obtained from slow evaporation of a concentrated hexamethyldisiloxane–hexanes mixture. The crystals were washed with two aliquots of cold hexamethyldisiloxane and dried. Yield: 313 mg (67%). Anal. calcd. for C<sub>37</sub>H<sub>57</sub>P<sub>2</sub>Si<sub>2</sub>Zr: C 56.18, H 7.26; found: C 56.15, H 7.31.

*Major isomer* (60%): <sup>1</sup>H NMR (20°C, C<sub>6</sub>D<sub>6</sub>)  $\delta$ : 0.27 and 0.46 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.84 and 1.28 (dd, 2H, <sup>2</sup>J<sub>HH</sub> = 15 Hz, <sup>2</sup>J<sub>PH</sub> = 4 Hz, SiCH<sub>2</sub>P), 0.80, 0.98, 1.04, and 1.13 (dd, 6H, <sup>3</sup>J<sub>HH</sub> = 7 Hz, <sup>3</sup>J<sub>PH</sub> = 7 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.74 and 2.53 (sept, 2H, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 6.75 (d, 2H, <sup>4</sup>J<sub>HH</sub> = 1 Hz, Cp-*H*), 6.86 (t, 1H, <sup>4</sup>J<sub>HH</sub> = 1 Hz, Cp-*H*), 7.00 (t, 2H, *p*-C<sub>6</sub>H<sub>5</sub>), 7.24 (t, 4H, *m*-C<sub>6</sub>H<sub>5</sub>), 7.45 (d, 4H, *o*-C<sub>6</sub>H<sub>5</sub>). <sup>31</sup>P NMR (20°C, C<sub>6</sub>D<sub>6</sub>)  $\delta$ : 9.3 (s).

*Minor isomer* (40%): <sup>1</sup>H NMR (20°C, C<sub>6</sub>D<sub>6</sub>)  $\delta$ : 0.21 and 0.33 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.67 and 1.14 (dd, 2H, <sup>2</sup>J<sub>HH</sub> = 14 Hz, <sup>2</sup>J<sub>PH</sub> = 5 Hz, SiCH<sub>2</sub>P), 0.75, 1.19, 1.29, and 1.35 (dd, 6H, <sup>3</sup>J<sub>HH</sub> = 7 Hz, <sup>3</sup>J<sub>PH</sub> = 7 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 2.10 and 2.15 (sept, 2H, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 6.46 (t, 1H, <sup>4</sup>J<sub>HH</sub> = 1 Hz, Cp-H), 6.80 (d, 2H, <sup>4</sup>J<sub>HH</sub> = 1 Hz, Cp-H), 6.94 (t, 2H, *p*-C<sub>6</sub>H<sub>5</sub>),

7.18 (t, 4H, *m*-C<sub>6</sub>H<sub>5</sub>), 7.35 (d, 4H, *o*-C<sub>6</sub>H<sub>5</sub>). <sup>31</sup>P NMR (20°C, C<sub>6</sub>D<sub>6</sub>)  $\delta$ : 6.9 (s).

#### **Concluding remarks**

In this paper a series of zirconium complexes stabilized by the ancillary P<sub>2</sub>Cp ligand are presented in which the formal oxidation state can be regarded as Zr(II). The ethylene complexes 2 and 4a react with CO via loss of ethylene to generate carbonyl derivatives, and 2a undergoes a similar reaction with diphenylacetylene to produce alkyne 7a. The slow reaction of the saturated 18-electron complex 4a with CO demonstrates that phosphine dissociation is required to provide a reactive site. The lack of reactivity of alkyne 7a with CO presumably originates from the same electronic saturation of that species. In comparison, the immediate incorporation of CO by the 16-electron ethylene complexes 2a or 2b suggests an associative mechanism. The displacement of a coordinated ethylene molecule by CO is a rare occurrence in early metal complexes (33). It might have been anticipated that strong back-bonding should confer a degree of Zr(IV) metallacycle character in the metal-ethylene bonding as shown in A; however, it is apparent from the resulting ligand substitution reactions that considerable Zr(II) character is still present in these ethylene derivatives.

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