

## Bimetallic complexes

# IV. <sup>1</sup> Synthesis, dynamic behavior and reactions of C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>-bridged Zr(II)–Mo(0) complexes

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Received 12 June 1997

### Abstract

The synthesis and reactions of bimetallic Zr(II)–Mo(0) complexes with bridging C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub> ligands (henceforth abbreviated as Cp') are described. Reaction of Cp'<sub>2</sub>ZrCl<sub>2</sub> (**1**) with *n*-butyllithium in THF produces a metastable material tentatively formulated as Cp'<sub>2</sub>Zr · 2 LiCl · 4 THF (**2**). Diphenyldisulfide instantaneously converts **2** into the Zr(IV) dithiolate Cp'<sub>2</sub>Zr(SPh)<sub>2</sub> (**3**). When **2** is treated with [Mo(CO)<sub>4</sub>(norbornadiene)], an unstable intermediate is formed which can be trapped in good yield with *tert*-butylisocyanide to give [Cp'<sub>2</sub>Zr(CN*t*-Bu)<sub>2</sub>Mo(CO)<sub>4</sub>] (**4**). Treatment of [Cp'<sub>2</sub>Zr(Cl)(Me)Mo(CO)<sub>3</sub>L] (L=CO (**5a**), PMe<sub>3</sub> (**5b**)) with cyclohexenyllithium in the presence of PMe<sub>3</sub> gives the corresponding binuclear cyclohexyne complexes [Cp'<sub>2</sub>Zr(PMe<sub>3</sub>)(C<sub>6</sub>H<sub>8</sub>)Mo(CO)<sub>3</sub>L] (**6a**, **b**). These complexes are fluxional on the NMR timescale due to a flip motion of the cyclohexyne ligand between two equivalent positions (Δ*G*<sup>‡</sup> = (40 ± 8) kJ/mol). Protonation in THF converts **6a** into the cyclohexenyl zirconium complex [Cp'<sub>2</sub>Zr(THF)(C<sub>6</sub>H<sub>9</sub>)Mo(CO)<sub>4</sub>]BPh<sub>4</sub> (**7**). Alkenes such as styrene, 4-chlorostyrene or norbornadiene give the expected insertion products **8a–c** which, due to their insufficient stability, could not be isolated. Stable insertion products were, however, obtained with ketones such as benzophenone (**9a**), 1,3-diphenylacetone (**9b**) and cyclohexanone (**9c**). © 1998 Elsevier Science S.A.

**Keywords:** Molybdenum; Zirconium; Alkyne complexes; Insertion reactions

## 1. Introduction

In the previous publications of this series, we have described several attempts to achieve the cooperative activation of polar molecules in the coordination sphere of C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>-bridged binuclear Zr(IV)–M(0) complexes (M = Mo, W) [1–3]. Although this turned out to be more difficult than anticipated, we have finally been able to demonstrate the coupling of two tungsten-bound nitrile ligands and a zirconium-bound methyl group to give a bridging 1,3-diiminato ligand [1].

The chemistry of d<sup>2</sup>-zirconocene complexes is in many respects quite different from their d<sup>0</sup>-congeners. Apart from being a strong reducing agent, the Zr(II) center has a pronounced tendency to bind soft Lewis bases, especially unsaturated systems such as alkenes or alkynes [4–10]. Many of these complexes undergo a

variety of interesting and synthetically useful insertion reactions with polar double bonds such as aldehydes, ketones, nitriles [8–10], and even metal-bound carbon monoxide [11]. Therefore, we expected that analogous binuclear Zr(II)–Mo(0) complexes would exhibit a similarly rich chemistry.

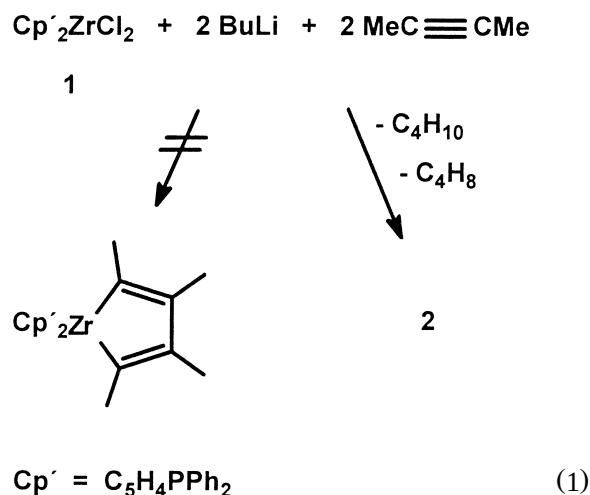
## 2. Results and discussion

### 2.1. Mononuclear zirconium complexes

Negishi et al. have developed a synthetically very useful route to reactive d<sup>2</sup>-zirconocene complexes: Treatment of zirconocene dichloride with *n*-butyllithium at low temperature produces an unstable intermediate, presumably dibutyl zirconocene, which upon warm up eliminates butane and butene. The highly reactive 'zirconocene equivalent' thus formed, adds a wide variety of unsaturated systems including dienes and alkynes [9,10].

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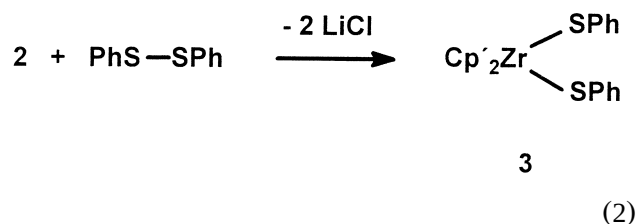
<sup>1</sup> For Part III, see Ref. [1].



Similar treatment of bis(diphenylphosphino)zirconocene dichloride (1) in THF with *n*-butyllithium in the presence of an excess of 2-butyne did, in our hands, not produce the expected zirconacyclopentadiene complex. Instead, a dark brown material (2) was obtained (Eq. (1)) which could be recrystallized from benzene/hexane. Elemental analyses and NMR spectra indicated a composition  $\text{Cp}'_2\text{Zr} \cdot 2 \text{ LiCl} \cdot 4 \text{ THF}$ . Identical material was obtained without the addition of 2-butyne or in the presence of  $\text{PMe}_3$  or *t*-BuNC, two ligands which would be expected to give isolable zirconocene complexes [4]. The  $^{31}\text{P}$  NMR spectrum of 2 exhibits a slightly broadened singlet at  $-19.0$  ppm which becomes sharp at  $0^\circ\text{C}$ . As monitored by  $^1\text{H}$

NMR, the THF can be quantitatively and reversibly exchanged for dimethoxyethane or 1,2-diphenyldimethoxyethane. The new adducts, however, do not crystallize well and could not be isolated in an analytically pure state. Although we do not know the precise nature of 2, it is reasonable to assume that it contains chloride bridges between Zr and Li similar to the crystallographically characterized complexes  $[(\text{Cp}_2\text{Ti})_2(\mu\text{-Cl})_4\text{Mg}(\text{THF})_2]$  [12],  $[(t\text{-BuC}_5\text{H}_4)_3\text{La}(\mu\text{-Cl})\text{Li}(\text{THF})_3]$  [13], and  $[\text{Cp}'_2\text{Yb}(\mu\text{-Cl})_2\text{Na}(\text{dme})_2]$  [14].

Evidence that 2 is a Zr(II) equivalent comes from the following observations. Treatment of 2 with diphenyldisulfide gives the known zirconocene dithiolate 3 [1] (Eq. (2)).



With tetracarbonyl(norbornadiene)molybdenum an instantaneous reaction (as monitored by  $^1\text{H}$  and  $^{31}\text{P}$  NMR) ensues followed by slow decomposition. However, when a small amount of *t*-BuNC is added to the reaction mixture right after the molybdenum complex has dissolved, then the binuclear isocyanide complex 4 can be isolated in good yield (Eq. (3)).

Table 1  
NMR spectroscopic data of binuclear complexes  $[\text{Cp}'_2\text{Zr}(\text{XY})\text{Mo}(\text{CO})_3\text{L}]$  (4–9)<sup>a</sup>

| No. | $^1\text{H}$ NMR ( $\text{C}_6\text{D}_6$ ) |                                                                                                   | $^{31}\text{P}$ NMR ( $\text{C}_6\text{D}_6$ )                        |
|-----|---------------------------------------------|---------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------|
|     | Cp'                                         | X, Y                                                                                              |                                                                       |
| 4   | 5.82, 6.28                                  | 0.86                                                                                              | 25.1                                                                  |
| 6a  | 5.06, 5.23, 5.85, 6.35                      | 0.59 <sup>b</sup> , 1.50 <sup>c</sup> , 1.67 <sup>c</sup> , 2.19 <sup>c</sup> , 2.83 <sup>c</sup> | $-0.5$ , 27.6 <sup>d</sup> , 28.6 <sup>d</sup>                        |
| 6b  | 5.20–6.10 <sup>e,f</sup>                    | 0.62 <sup>g</sup> , 1.80 <sup>c</sup> , 1.93 <sup>c</sup> , 2.34 <sup>c</sup> , 3.10 <sup>c</sup> | $-0.4$ , 25.0 <sup>h</sup> , 29.3 <sup>h</sup> , $-27.2$ <sup>h</sup> |
| 7   | 5.97, 6.47, 6.79                            | 1.51 <sup>i</sup> , 1.90 <sup>i</sup> , 5.78 <sup>i</sup> , 1.41 <sup>k</sup> , 3.52 <sup>k</sup> | 31.5                                                                  |
| 8a  |                                             |                                                                                                   | 30.6, 30.8 <sup>l</sup>                                               |
| 8b  |                                             |                                                                                                   | 30.9, 31.2 <sup>l</sup>                                               |
| 8c  |                                             |                                                                                                   | 30.1, 30.6 <sup>l</sup>                                               |
| 9a  | 5.53, 5.92, 6.56, 6.86                      | 1.45 <sup>c</sup> , 1.52 <sup>c</sup> , 1.92 <sup>c</sup> , 2.00 <sup>c</sup>                     | 27.8                                                                  |
| 9b  | 5.65, 5.91, 6.42, 6.44                      | 1.67 <sup>c</sup> , 1.80 <sup>c</sup> , 1.90 <sup>c</sup> , 2.12 <sup>c,m</sup>                   | 29.6                                                                  |
| 9c  | 5.53, 5.70, 6.45, 6.69                      | 1.00–2.10 <sup>n</sup>                                                                            | 28.2                                                                  |

<sup>a</sup>Aryl signals in the 6.5–8.0 ppm region are uncharacteristic and have been omitted. For further data, see Section 4.

<sup>b,d</sup>  $^2J(\text{P-H}) = 6$  Hz, Zr– $\text{PMe}_3$ .

<sup>c,m</sup>  $\text{C}_6\text{H}_8$ .

<sup>d</sup>At 203 K, AB-system,  $^2J(\text{P-P}) = 28$  Hz.

<sup>e,m</sup> Not resolved.

<sup>f</sup>0.69 (d,  $^2J(\text{P-H}) = 7$  Hz, Mo– $\text{PMe}_3$ ).

<sup>g,d</sup>  $^2J(\text{P-H}) = 6$  Hz, Zr– $\text{PMe}_3$ .

<sup>h</sup>At 203 K, t,  $^2J(\text{P-P}) = 27$  Hz.

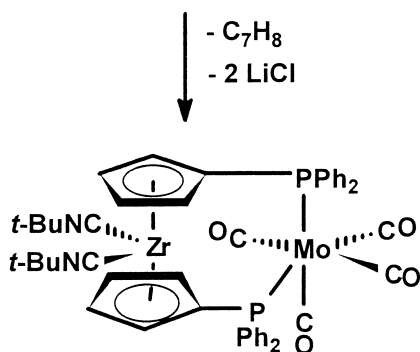
<sup>i,m</sup> ( $\text{C}_6\text{H}_9$ ).

<sup>k</sup>m (THF).

<sup>l</sup>AB-system,  $^2J(\text{P-P}) = 28$  Hz.

<sup>m</sup>2.68, 3.11 (AB-system,  $^2J(\text{H-H}) = 16$  Hz,  $\text{CH}_2\text{Ph}$ ).

<sup>n</sup>m, not resolved,  $\text{CH}_2$ .



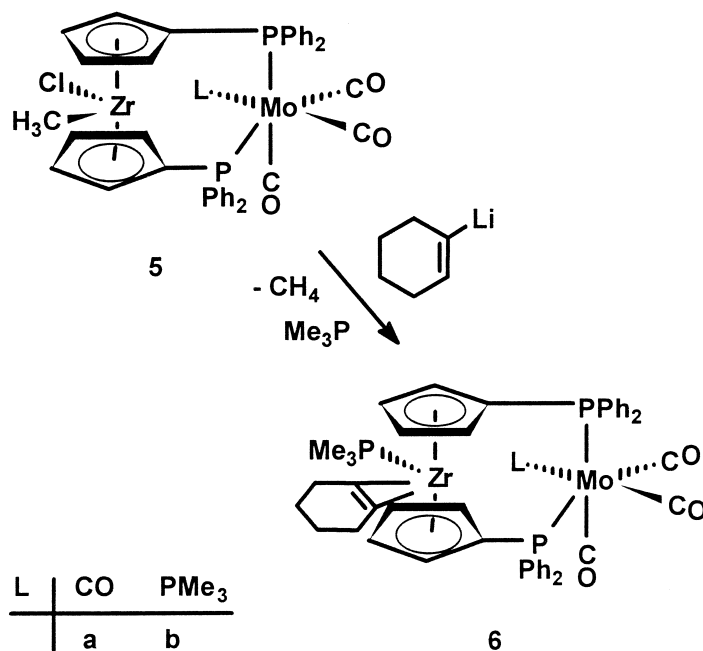
(3)

**4** is a yellow, air-stable crystalline compound which is soluble in the common organic solvents except

aliphatic hydrocarbons. Its infrared spectrum exhibits the typical pattern of a *cis*-[Mo(CO)<sub>4</sub>L<sub>2</sub>] complex and, in addition, two strong  $\nu(\text{CN})$  vibrations of the isocyanide ligands. The <sup>1</sup>H NMR spectrum consists of a sharp singlet at 0.86 ppm for the *t*-butyl groups and two multiplets for the Cp' protons indicating that the molecule has mirror symmetry. The phosphorus resonance occurs at 25.1 ppm, the typical region for a Cp' ligand bridging a Zr and a Mo atom [1–3].

## 2.2. Binuclear zirconium–molybdenum complexes

The metathesis of methyl(chloro)zirconocene with alkenyllithium reagents is a proven route to zirconocene complexes of alkynes [8,15], including cyclohexyne [16]. Analogously, the binuclear complexes **5a, b** [1], upon treatment with cyclohexenyllithium and trimethylphosphine give the cyclohexyne complexes **6a, b** (Eq. (4)).



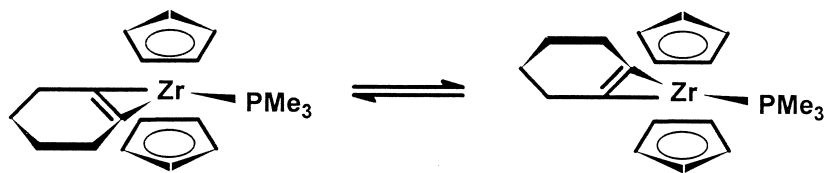
(4)

**6a, b** were isolated as air-sensitive brownish-yellow microcrystalline powders. Their infrared spectra exhibit the expected  $\nu(\text{CO})$  pattern of the *cis*-[Mo(CO)<sub>4</sub>] (**6a**) and *fac*-[Mo(CO)<sub>3</sub>] (**6b**) unit, respectively. At room temperature, the <sup>1</sup>H and <sup>31</sup>P NMR spectra are broadened indicating that the molecules are fluxional. The <sup>31</sup>P NMR spectrum of **6a** at 203 K consists of an AB-system for the Mo-bound PPh<sub>2</sub> groups and a sharp singlet for the Zr-bound PMe<sub>3</sub> ligand (Table 1).

While the AB system collapses to a singlet upon warm up (coalescence at 240 K), the PMe<sub>3</sub> signal remains virtually unaffected, even in the presence of added PMe<sub>3</sub>. Simulation of the spectra [17,18] applying a two-site exchange model [19] yields a free energy of activation of (40 ± 8) kJ/mol. Similar observations can be made for **6b** whose Mo-bound PPh<sub>2</sub> groups are exchange-equivalent at ambient temperature but become

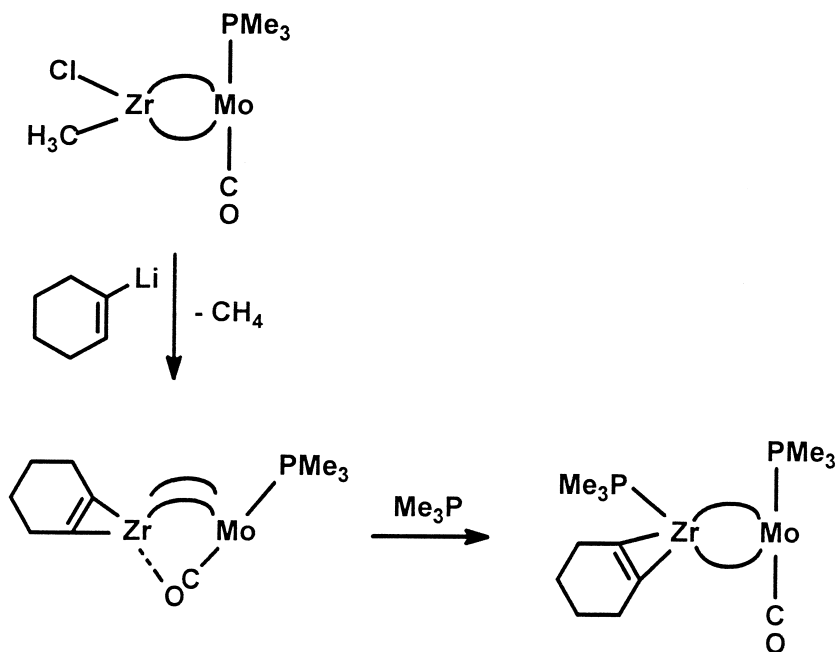
nonequivalent upon cooling. Based on the known structure of the mononuclear analog Cp<sub>2</sub>Zr(PMe<sub>3</sub>)(cyclohexyne) [16], this dynamic process is most likely described as a flip of the alkyne moiety between two equivalent positions as outlined in Scheme 1. That this motion is much slower in the binuclear complexes **6a, b** than in analogous mononuclear compounds is certainly due to the rigidity brought into the system by tying the two Cp' ligands to a second metal center.

The stereochemistry of the reaction described by Eq. (4) deserves some comment. While the starting compound **5b** is a 1:1 mixture of two diastereoisomers, the corresponding product **6b** is obtained as a single isomer. Two explanations might be given for this observation. First, the mobility of the coordination sphere around zirconium allows for a ready site exchange of the cyclohexyne and trimethylphosphine ligands, with one



$$\Delta G^\ddagger = (40 \pm 8) \text{ kJ/mol}$$

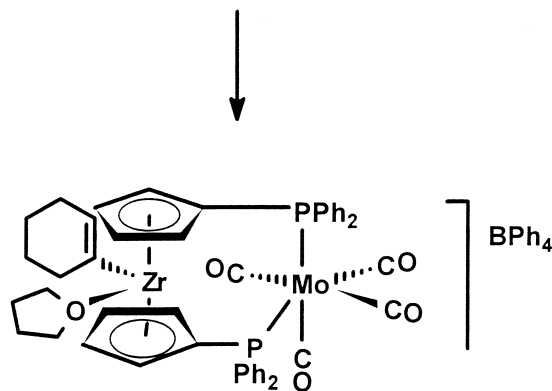
Scheme 1.



Scheme 2.

diastereomer being strongly favored. Given the small size of  $\text{PMe}_3$  and the quite large separation of the two metal centers, this seems to be quite unlikely. Secondly, the intermediate, coordinatively unsaturated zirconium-cyclohexyne complex<sup>2</sup> is temporarily stabilized by a  $\text{Zr-OC-Mo}$  bridge which is opened stereospecifically upon addition of  $\text{PMe}_3$  (Scheme 2).

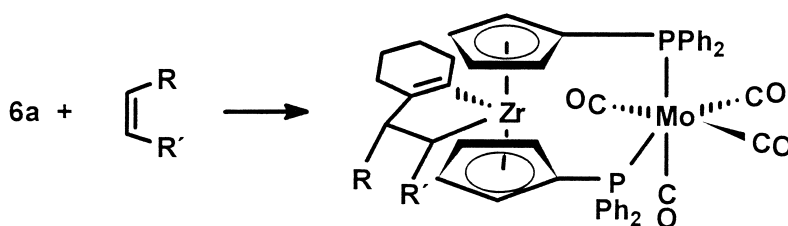
Ligand substitution reactions at both  $d^0$  and  $d^2$ -zirconocene complexes are known to proceed by an associative mechanism [22,23]. However, the question of the stereochemical course has, to our knowledge, not yet been addressed.



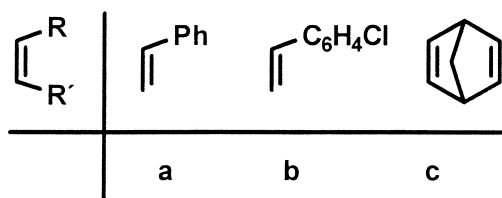
<sup>2</sup> Zirconocene-alkyne complexes without additional ligands have recently been characterized (Refs. [20,21]).

Protonation of **6a** using the weak Brønsted acid  $[\text{PhMe}_2\text{NH}]\text{BPh}_4$  in THF gives the cationic cyclohexenyl complex **7** (Eq. (5)). The vacant coordination site thus created at zirconium takes up a molecule of THF rather than a Mo-bound carbonyl group. This is apparent from the IR spectrum in the  $\nu(\text{CO})$  region which shows the typical pattern of an unperturbed *cis*- $[\text{Mo}(\text{CO})_4]$  moiety. Carrying out the reaction in non-co-

ordinating solvents led to decomposition instead of the expected formation of a Zr–OC–Mo bridge [24,25]. Apparently, the electron density at the oxygen atoms of a formally neutral molybdenum tetracarbonyl is not high enough for the formation of a stable zirconium–oxygen linkage, even in the presence of two  $\text{C}_5\text{H}_4\text{PPh}_2$  ligands acting as additional braces.



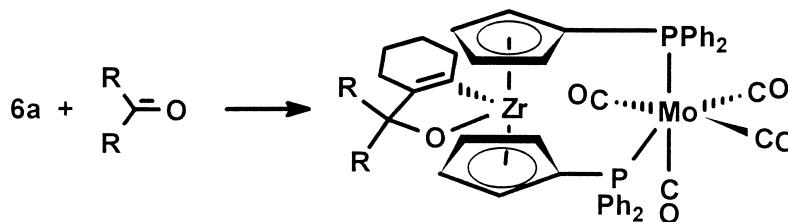
8a - c



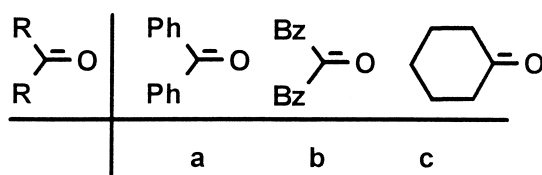
(6)

Zirconocene alkyne complexes undergo a variety of insertion reactions with alkenes, alkynes, aldehydes, ketones, nitriles, and other unsaturated systems [8]. **6a** similarly adds styrene, 4-chlorostyrene or norbornadiene as shown by  $^{31}\text{P}$  NMR (Eq. (6)). Within 1 h at room temperature, the singlet of **6a** is cleanly replaced by

narrow AB systems arising from the addition products **8a–c**, respectively. Any attempts at their isolation, however, led to extensive decomposition, inter alia to the zirconium-free complex  $[\text{Mo}(\text{CO})_4((\text{Ph}_2\text{P})_2(\text{C}_{10}\text{H}_{10}))]$  [1,26].



9a - c



(7)

Perfectly stable cycloadducts, however, were formed in the reaction of **6a** with ketones (Eq. (7)). **9a–c** are yellow air-stable, crystalline solids. Their  $^1\text{H}$  NMR spectra show signals for all groups present in the expected intensity ratio. The unsymmetrical coordination environment of the zirconium center is evident from the nonequivalence of all four protons of each  $\text{Cp}'$  ligand as well as the diastereotopicity of the benzylic protons of **9b**. In the  $^{13}\text{C}$  NMR spectra all signals can be readily assigned. Conclusive evidence for the proposed constitution of **9a–c** comes from two signals at 160 and 185 ppm which are typical for zirconium-bound vinyl groups [16]. Compared to the alkene adducts **8a–c** it is certainly the thermodynamic strength of the  $\text{Zr–O}$  bond which adds to the stability of **9a–c**.

### 3. Conclusions

The chemistry of  $\text{PPh}_2$ -substituted zirconocenes as well as their ligand-bridged binuclear derivatives does not always mirror that of the parent  $\text{C}_5\text{H}_5$  complexes. Likely reasons for this different behavior are the shielding of the coordination sphere of zirconium by the large  $\text{PPh}_2$  groups and the reduction of the flexibility of the complex brought about by tying the  $\text{C}_5\text{H}_4\text{PPh}_2$  ligands to a second metal atom. Nevertheless, binuclear  $d^2$ – $d^6$  systems are readily accessible and, by and large, exhibit the expected reactivity pattern. In addition, the presence of a suitably substituted  $d^6$ -metal center seems to offer a chance to gain some insight into the stereochemistry of ligand substitution reactions at pseudotetrahedral metallocene complexes.

### 4. Experimental

All manipulations were carried out in Schlenk-type glassware under an atmosphere of purified nitrogen or argon. Solvents were dried and distilled under nitrogen prior to use. NMR solvents were degassed and stored under nitrogen over molecular sieves. NMR: Bruker AMX 400; chemical shifts are reported in ppm vs. TMS ( $^1\text{H}$ ,  $^{13}\text{C}$ ) and 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ). IR: Bruker IFS 25, Perkin-Elmer 283.

The following starting materials were prepared by published procedures:  $\text{Cp}'_2\text{ZrCl}_2$  (**1**) [27],  $[\text{Mo}(\text{CO})_4(\text{norbornadiene})]$  [28],  $\text{PMe}_3$  [29],  $[\text{PhMe}_2\text{NH}]\text{BPh}_4$  [30],  $\text{LiC}_6\text{H}_9$  [16],  $[\text{Cp}'_2\text{Zr}(\text{Cl})(\text{Me})\text{Mo}(\text{CO})_3\text{L}]$  ( $\text{L}=\text{CO}$  (**5a**),  $\text{PMe}_3$  (**5b**)) [1]. All other reagents were used as obtained commercially.

#### 4.1. $\text{Cp}'_2\text{Zr} \cdot 2 \text{LiCl} \cdot 4 \text{THF}$ (**2**)

To a solution of  $\text{Cp}'_2\text{ZrCl}_2$  (0.40 g, 0.61 mmol) in THF (20 ml) is added at  $-70^\circ\text{C}$  a solution of *n*-butyllithium in hexane (0.8 ml, 2.0 mmol). The reaction mixture turns dark immediately. After 15 h at room

temperature, the solvent is removed under vacuum and the remaining residue is washed with pentane until a brown powder is obtained. This is dissolved in benzene, the solution is filtered over Celite, and the product isolated after evaporation. Yield: 0.37 g (63%), brown microcrystalline powder. Anal. found: C, 61.00; H, 5.31.  $\text{C}_{50}\text{H}_{60}\text{Cl}_2\text{Li}_2\text{O}_4\text{P}_2\text{Zr}$  (962.98) calcd.: C, 62.36; H, 6.28.

#### 4.2. Reaction of **2** with diphenyldisulfide

A solution of **2** (0.13 g, 0.14 mmol) in benzene (15 ml) is treated with diphenyldisulfide (30 mg, 0.14 mmol). After 20 min, the solution is filtered and partially evaporated and the product precipitated by adding pentane. NMR analysis ( $^1\text{H}$ ,  $^{31}\text{P}$ ) reveals the formation of two products, the major one being the dithiolate **3** [1].

#### 4.3. $[\text{Cp}'_2\text{Zr}(\text{t-BuNC})_2\text{Mo}(\text{CO})_4]$ (**4**)

To a solution of **2** (0.10 g, 0.10 mmol) in benzene (2.0 ml) is added at room temp.  $[\text{Mo}(\text{CO})_4(\text{norbornadiene})]$  (30 mg, 0.10 mmol) and, after 2 min, *tert*-butyl isonitrile (50  $\mu\text{l}$ , 0.55 mmol). After 1 h, the mixture is taken to dryness and the residue recrystallized from a small amount of benzene/pentane. Yield: 63 mg (65%), brownish-yellow crystalline powder, m.p.  $77^\circ\text{C}$  (dec.). IR (Nujol): 2162(m), 2136(m)  $\text{cm}^{-1}$  (CN); 2012(m), 1896(vs, br)  $\text{cm}^{-1}$  (CO). Anal. found: C, 61.08; H, 4.82; N, 2.67.  $\text{C}_{48}\text{H}_{46}\text{MoN}_2\text{O}_4\text{P}_2\text{Zr}$  (964.01) calcd.: C, 59.80; H, 4.81; N, 2.91.

#### 4.4. $[\text{Cp}'_2\text{Zr}(\text{PMe}_3)(\text{C}_6\text{H}_8)\text{Mo}(\text{CO})_4]$ (**6a**)

To a solution of **5a** (0.17 g, 0.20 mmol) in THF (5.0 ml) are added at  $-70^\circ\text{C}$  cyclohexenyllithium in ether (0.20 mmol) and  $\text{PMe}_3$  (0.20 ml, 2.20 mmol). Upon warming to room temperature some gas evolution is observed. The product is isolated by filtration, partial evaporation, and careful addition of pentane. Yield: 0.15 g (79%), brownish-yellow crystalline powder, m.p.  $85^\circ\text{C}$  (dec.). IR (Nujol): 2013(m), 1915(s), 1897(vs), 1873(sh)  $\text{cm}^{-1}$  (CO). Anal. found: C, 59.47; H, 4.92.  $\text{C}_{47}\text{H}_{45}\text{MoO}_4\text{P}_3\text{Zr}$  (953.96) calcd.: C, 59.18; H, 4.75.

#### 4.5. $[\text{Cp}'_2\text{Zr}(\text{PMe}_3)(\text{C}_6\text{H}_8)\text{Mo}(\text{CO})_3\text{PMe}_3]$ (**6b**)

This compound was obtained from **5b** as described above. Yield: 0.17 g (86%), brownish-yellow crystalline powder, m.p.  $63^\circ\text{C}$  (dec.). IR (Nujol): 1933(s), 1830(vs)  $\text{cm}^{-1}$  (CO). Anal. found: C, 59.70; H, 5.28.  $\text{C}_{49}\text{H}_{54}\text{MoO}_3\text{P}_4\text{Zr}$  (1002.02) calcd.: C, 58.74; H, 5.43.

#### 4.6. $[\text{Cp}'_2\text{Zr}(\text{THF})(\text{C}_6\text{H}_9)\text{Mo}(\text{CO})_4]\text{BPh}_4$ (**7**)

To a solution of **6a** (0.24 g, 0.24 mmol) in THF (10.0 ml) is added dimethylanilinium tetraphenylborate (0.11 g, 0.25 mmol) at  $-70^\circ\text{C}$ . The mixture is allowed to

warm to  $-20^{\circ}\text{C}$  and the product is isolated after cold filtration and partial evaporation by adding pentane. Yield: 0.19 g (63%), brownish-yellow crystalline powder, m.p.  $126^{\circ}\text{C}$  (dec.).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 25.4, 25.5, 27.8, 35.5$  (s,  $\text{CH}_2$ ),  $25.9, 68.6$  (s, THF),  $114.3, 116.2, 118.0, 122.8, 123.7$  (s, br,  $\text{C}_5\text{H}_4$ ),  $122.2, 126.1, 128.4, 128.7, 130.0, 130.7, 133.2, 134.3, 136.3, 137.8, 138.3$  (phenyl resonances),  $138.7$  (s,  $\text{C}=\text{C}-\text{Zr}$ ),  $164.4$  (q,  $^1J(\text{C}-\text{B}) = 37$  Hz,  $\text{B}-\text{C}$ ),  $191.6$  (s,  $\text{C}=\text{C}-\text{Zr}$ ),  $210.2$ , (t,  $^2J(\text{P}-\text{C}) = 9$  Hz, CO),  $210.8$  (t,  $^2J(\text{P}-\text{C}) = 9$  Hz, CO),  $214.6$  (t, outer lines not resolved, CO). IR (Nujol):  $2016(\text{m}), 1898(\text{vs}, \text{br}) \text{ cm}^{-1}$  (CO). Anal. found: C, 68.29; H, 5.03.  $\text{C}_{72}\text{H}_{65}\text{BMoO}_5\text{P}_2\text{Zr}$  (1270.23) calcd.: C, 68.08; H, 5.16.

#### 4.7. $[\text{Cp}'_2\text{Zr}(\text{OCPh}_2\text{C}_6\text{H}_8)\text{Mo}(\text{CO})_4]$ (**9a**)

To a solution of **6a** (0.10 g, 0.10 mmol) in benzene (5.0 ml) is added benzophenone (20 mg, 0.11 mmol). After stirring 2 h at room temperature, the solution is partially evaporated and the product precipitated by adding pentane. Yield: 87 mg (82%), yellow crystalline powder, m.p.  $133^{\circ}\text{C}$  (dec.).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 23.7, 25.0, 32.1, 35.5$  (s,  $\text{CH}_2$ ),  $95.3$  (s,  $\text{OCPh}_2$ ),  $110.9, 118.9, 119.3, 120.3, 121.1$  (s, br,  $\text{C}_5\text{H}_4$ ),  $132-140$  (m, phenyl resonances),  $158.9$  (s,  $\text{C}=\text{C}-\text{Zr}$ ),  $185.0$  (t, outer lines not resolved,  $\text{C}=\text{C}-\text{Zr}$ ),  $211.0$  (t,  $^2J(\text{P}-\text{C}) = 9$  Hz, CO),  $213.9$  (t, outer lines not resolved, CO). Anal. found: C, 64.07; H, 4.29.  $\text{C}_{57}\text{H}_{46}\text{MoO}_5\text{P}_2\text{Zr}$  (1060.10) calcd.: C, 64.58; H, 4.37.

#### 4.8. $[\text{Cp}'_2\text{Zr}(\text{OC}(\text{CH}_2\text{Ph})_2\text{C}_6\text{H}_8)\text{Mo}(\text{CO})_4]$ (**9b**)

This compound was obtained from **6a** and diphenylacetone as described above. Yield: 84 mg (77%), yellow crystalline powder, m.p.  $97^{\circ}\text{C}$  (dec.).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 23.7, 25.3, 30.0, 35.2$  (s,  $\text{CH}_2$ ),  $45.0$  (s,  $\text{CH}_2\text{Ph}$ ),  $94.0$  (s,  $\text{OC}(\text{CH}_2\text{Ph})_2$ ),  $113.0, 118.6, 118.9, 120.2, 121.6$  (s, br,  $\text{C}_5\text{H}_4$ ),  $132-140$  (m, phenyl resonances),  $157.4$  (s,  $\text{C}=\text{C}-\text{Zr}$ ),  $185.3$  (s,  $\text{C}=\text{C}-\text{Zr}$ ),  $210.7$ , (t,  $^2J(\text{P}-\text{C}) = 8$  Hz, CO),  $212.1$  (t,  $^2J(\text{P}-\text{C}) = 8$  Hz, CO),  $214.2$  (t, outer lines not resolved, CO). Anal. found: C, 65.12; H, 4.20.  $\text{C}_{59}\text{H}_{50}\text{MoO}_5\text{P}_2\text{Zr}$  (1088.15) calcd.: C, 65.12; H, 4.63.

#### 4.9. $[\text{Cp}'_2\text{Zr}(\text{OC}_6\text{H}_{10}\text{C}_6\text{H}_8)\text{Mo}(\text{CO})_4]$ (**9c**)

This compound was obtained from **6a** and cyclohexanone as described above. Yield: 66 mg (68%), yellow crystalline powder, m.p.  $108^{\circ}\text{C}$  (dec.).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta = 21.2, 23.1, 24.9, 25.3, 27.5, 33.9, 34.3$  (s,  $\text{CH}_2$ ),  $89.2$  (s,  $\text{OCC}_5\text{H}_{10}$ ),  $109.6, 117.2, 117.6, 119.6, 119.8$ , (s, br,  $\text{C}_5\text{H}_4$ ),  $131-139$  (m, phenyl resonances),  $160.4$  (s,  $\text{C}=\text{C}-\text{Zr}$ ),  $178.9$  (s,  $\text{C}=\text{C}-\text{Zr}$ ),  $209.2, 209.9, 213.1$  (t, not resolved, CO). Anal. found: C,

61.98; H, 4.54.  $\text{C}_{50}\text{H}_{46}\text{MoO}_5\text{P}_2\text{Zr}$  (976.02) calcd.: C, 61.53; H, 4.75.

## Acknowledgements

We are indebted to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for the generous support of this work.

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