

Preparation, characterization and carbonylation of the ring-functionalized dibenzyl zirconocenes, $(\eta^5\text{-C}_5\text{H}_5)_x((\eta^5\text{-C}_5\text{H}_4)\text{P}(\text{C}_6\text{H}_5)_2)_{2-x}\text{Zr}(\text{CH}_2\text{C}_6\text{H}_5)_2$ ($x = 1$, (**1**); $x = 0$, (**2**))

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Abstract

The preparation, characterization and carbonylation products of the ring-functionalized alkyl zirconocenes, $(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{-P}(\text{C}_6\text{H}_5)_2)\text{Zr}(\text{CH}_2\text{C}_6\text{H}_5)_2$ (**1**), $(\eta^5\text{-C}_5\text{H}_4\text{-P}(\text{C}_6\text{H}_5)_2)_2\text{Zr}(\text{CH}_2\text{C}_6\text{H}_5)_2$ (**2**) are described. These compounds insert one molecule of CO to give products which interconvert between an acyl form and a phosphonium-alkoxide form at ambient temperatures via a reversible nucleophilic attack of the phosphine at the carbenium-like η^2 -acyl carbon as shown through variable-temperature ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR studies.

Keywords: Zirconium; Carbonylation; Metallocenes; Acyl derivatives

1. Introduction

We have previously investigated the preparation and carbonylation of bis-ring-functionalized zirconocenes, bis((diphenylphosphino-cyclopentadienyl)dimethyl zirconium(IV) and bis((diphenylphosphino-cyclopentadienyl)chloromethyl zirconium(IV) [1] and mono-ring functionalized zirconocenes of type A ($\text{R} = \text{CH}_3$; $\text{X} = \text{CH}_3$ or Cl) shown in Fig. 1 [2].

Carbonylation of alkyl complexes A results in acyl complexes which are in equilibrium with a phosphonium-alkoxide complex as shown in B (Fig. 1). The structure of the phosphonium-alkoxide form has been characterized by X-ray crystallography [1]. The susceptibility of the acyl carbon to nucleophilic attack by the phosphorus led us to consider nucleophilic attack of the prochiral carbenium-like acyl carbon with external nucleophiles. In preparation for exploring this possibility, complexes with the stereochemical probes such as the benzyl group were needed. The preparation, characterization and carbonylation reactions of $(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{-P}(\text{C}_6\text{H}_5)_2)\text{Zr}(\text{CH}_2\text{C}_6\text{H}_5)_2$ (**1**) and $(\eta^5\text{-C}_5\text{H}_4\text{-P}(\text{C}_6\text{H}_5)_2)_2\text{Zr}(\text{CH}_2\text{C}_6\text{H}_5)_2$ (**2**) (where prochiral **1** bears diastereotopic protons on the methylene group) are reported here.

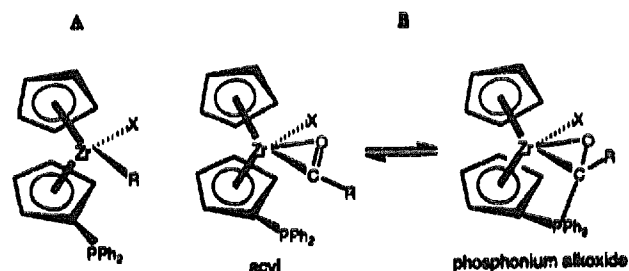
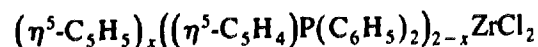


Fig. 1. Structures of A and B.

$\text{P}(\text{C}_6\text{H}_5)_2)_2\text{Zr}(\text{CH}_2\text{C}_6\text{H}_5)_2$ (**2**) (where prochiral **1** bears diastereotopic protons on the methylene group) are reported here.

2. Results and discussion

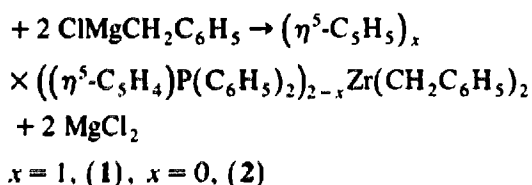
The preparations of **1** and **2** were accomplished through interaction of two equivalents of alkyl magnesium halide with the parent dichloro-ring-functionalized zirconocene [3] suspended in ether.



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Table 1
 ^1H NMR and $^{31}\text{P}\{^1\text{H}\}$ NMR data in CD_2Cl_2 for complexes 1 and 2

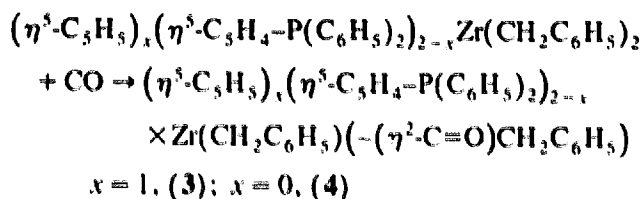
| Complex | C_5H_5 | C_5H_4 | $\text{CH}_2\text{-R}$ | $\text{P}(\text{C}_6\text{H}_5)_2$ | $\text{CH}_2\text{-C}_6\text{H}_5$ | ^{31}P |
|---------|------------------------|--|--|------------------------------------|--|---------------------|
| 1 | δ 5.90 (s) | δ 6.03 (m) δ 6.07 (m) | δ 1.70 (d, 10.8 Hz) δ 1.67 (d, 10.8 Hz) | δ 7.38 (m) | <i>o</i> - δ 6.69 <i>p</i> - δ 6.81 <i>m</i> - δ 7.13 | δ -19.13 (s) |
| 2 | n/a | δ 5.89 (m) δ 6.02 (m) | δ 1.50 (s) | δ 7.34 (m) | <i>o</i> - δ 6.54 <i>p</i> - δ 6.78 <i>m</i> - δ 7.08 | δ -19.43 (s) |



Removal of the solvent and extraction of the resulting residue with pentane gave uniformly good yields (greater than 80%) of the complexes. Analytical data were consistently low in C even with the use of combustion aids but gave good agreement for %H and %P. ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR data are summarized in Table 1. The $^{31}\text{P}\{^1\text{H}\}$ chemical shifts of the phosphine P atoms of 1 and 2 are nearly identical. The proton NMR spectra are unremarkable; it should be noted that in complex 2, a singlet was observed for the methylene protons, whereas in 1 they are diastereotopic and give rise to two doublets ($^2J_{\text{H-H}} = 10.8$ Hz in CD_2Cl_2), similar to that observed in other mono-functionalized zirconocene benzyl complexes [4].

Treating dichloromethane solutions of 1 or 2 with CO (0.3 atm) results in an immediate deepening of color consistent with the carbonylation of other ring-functionalized zirconocenes [1,2,5]. The products were quite soluble in dichloromethane and ether solvents, but much less so in aliphatic or aromatic hydrocarbons. Proton and phosphorus NMR spectra showed complete

consumption of starting material after about 20 min at ambient temperature to give only the carbonylated product. The NMR data were consistent with insertion of CO into the Zr-benzyl bond. Unlike the carbonylated dimethyl complexes which decompose upon removal of solvent [1], analytically pure samples of these complexes can be isolated in modest yields from dichloromethane-ether mixtures (ca. 30–50% isolated; however, the residue obtained from the mother liquor consists mainly of the carbonylation product as determined by NMR). Use of aliphatic precipitating solvents leads to the formation of oils. Multinuclear NMR spectroscopy and C/H/P analyses (with the exception of C) of the solids were consistent with formulation as the CO insertion product. We have found that carbon analyses were low for compounds of this sort, even when NMR spectra show no impurities and combustion aids were used [1,2].



Ambient temperature proton and phosphorus NMR suggested that fluxional behavior was present and a

Table 2
 ^1H NMR and $^{31}\text{P}\{^1\text{H}\}$ NMR data in CD_2Cl_2 for complexes 3 and 4 at 210 K

| Complex | C_5H_5 | C_5H_4 | $\text{CH}_2\text{-R}$ | $\text{P}(\text{C}_6\text{H}_5)_2$ | $\text{CH}_2\text{-C}_6\text{H}_5$ | ^{31}P |
|---------|------------------------|--|---|--|--|---|
| 3 | δ 5.81 (s) | δ 4.89 (m) δ 5.79 (m) δ 5.84 (m) δ 6.11 (m) | δ 1.71 (d, 8.6 Hz) δ 2.32 (d, 8.6 Hz) -CO- CH_2R δ 2.55 (dod, $J_{\text{P-H}} = 39$ Hz, $J_{\text{H-H}} = 14$ Hz) δ 3.25 (d, 14 Hz) | δ 7.25 (m) δ 7.49 (m) δ 7.68 (m) δ 7.78 (m) | δ 6.64 (t) δ 7.03 (m) δ 7.12 (d) δ 7.47 (m) | δ 12.80 (s) |
| 4 | n/a | δ 4.64 (m) δ 5.09 (m) δ 5.75 (m) δ 5.94 (m) δ 6.09 (m) δ 6.11 (m) δ 6.17 (m) δ 6.42 (m) | δ 0.91 (d, 8.3 Hz) δ 1.79 (d, 8.3 Hz) -CO- CH_2R δ 2.55 (dod, $J_{\text{P-H}} = 39$ Hz, $J_{\text{H-H}} = 14$ Hz) δ 3.18 (d, 14.5 Hz) | δ 7.25 (m) δ 7.50 (m) δ 7.62 (m) δ 7.70 (m) | δ 6.45 (m) δ 6.8 (m) δ 7.00 (m) δ 7.10 (m) | δ 12.48 (s) δ -19.71 (s) |

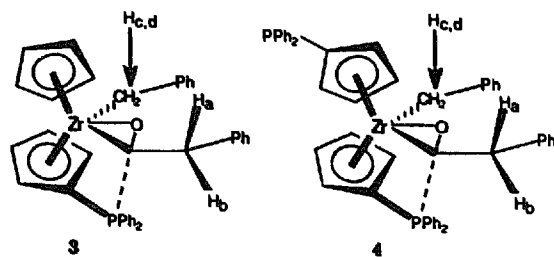


Fig. 2. Proposed structures of complexes 3 and 4.

multinuclear variable-temperature NMR study was performed. Data for low temperature and high temperature limiting spectra are listed in Tables 2 and 3. Fig. 2 shows the proposed structures for the carbonylated species where the dashed lines indicate the positions of bonds broken and formed in the fluxional process.

The diastereotopic protons H_a , H_b , H_c and H_d are not equivalent in these structures and indeed four signals were observed for these protons at low temperatures (less than -50°C). The regions containing these signals were quite similar for complexes 3 and 4. The diastereotopic $-(\text{C}-\text{O})-\text{CH}_2$ protons give rise to a doublet and a doublet of doublets; the additional splitting of one signal was due to coupling to the phosphorus atom bound to the carbon derived from CO. In complex 3, only one signal was observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR at δ 14.7 indicative of the phosphonium nature of the phosphorus atom. In complex 4, two signals were observed; one for the phosphonium phosphorus (δ 14.7) and one for the non-bound phosphine (δ -22.4). Use of ^{13}C O to form 3 gave a doublet for the phosphonium-alkoxide carbon at δ 39.3 ($J_{\text{C}-\text{P}} = 39.0$ Hz at 213 K) which broadened and shifted downfield with increasing temperature, and did not sharpen at the highest temperatures used in this study.

At higher temperatures, the spectra of 3 and 4 were quite different. The $^{31}\text{P}\{^1\text{H}\}$ NMR at 310 K of complex 3 shows a broad signal at δ 4.6 and complex 4 shows a single broad signal at δ -4.5. There were only two signals of equal area in complex 4 in the proton spec-

trum at 310 K, a singlet (protons c and d) and a doublet of triplets (protons a and b, ($J_{\text{H}-\text{H}} = 14$ Hz and $J_{\text{P}-\text{H}} = 10$ Hz)). In 3, H_a and H_b were inequivalent through temperatures up to 310 K, as two signals were observed throughout the temperature range with diastereotopic coupling of 14 Hz, although $J_{\text{P}-\text{H}}$ has decreased (29 Hz at 310 K compared with 39 Hz at 210 K). Protons c and d give separate signals in 3 with coupling constants ca. 9 Hz at all temperatures studied due to the lack of a phosphine group on the 'upper' cyclopentadienyl ring.

We interpret these results as supporting a rapid initial lateral insertion of CO into the Zr-C bond as observed by other workers [6] and supported by theoretical studies [7–9]. The chemical shifts of the alkyl groups at the high temperature limit were similar to that observed by Floriani and coworkers in the carbonylation of dibenzyl zirconocene [10,11]. The acyl group then undergoes intramolecular attack by the phosphine group(s) to give a phosphonium alkoxide which is in equilibrium with the acyl form. Comparison of the P-H coupling constants at the low and high temperature limits shows that the P is bonded to the acyl carbon about 74% of the time at room temperature for 3. The phosphonium alkoxide form of both 3 and 4 is favored at ambient temperatures but exchange between the two forms is rapid at ambient temperatures and above.

3. Conclusions

This work has shown that CO readily inserts into the zirconium-carbon bond of the ring-functionalized benzyl zirconocenes 1 and 2. The phosphine groups are involved in a fluxional nucleophilic attack of the acyl carbon of a transiently formed acyl species, leading to a phosphonium-alkoxide complex that is observed at low temperatures in fluid solution and isolated as solids. The facile attack by phosphorus seen here, and other observations that the C atom of a zirconocene acyl is susceptible to nucleophilic attack (both experimental [10–20] and theoretical [7,9,21]), intrigues us. Further work on

Table 3
 ^1H NMR and $^{31}\text{P}\{^1\text{H}\}$ NMR data in CD_2Cl_2 for complexes 3 and 4 at 310 K

| Complex | C_5H_5 | C_5H_4 | CH_2-R | $\text{P}(\text{C}_6\text{H}_5)_2$ | $\text{CH}_2-\text{C}_6\text{H}_5$ | ^{31}P |
|---------|------------------------|------------------------|---|------------------------------------|------------------------------------|---------------------------------------|
| 3 | δ 5.70 (s) | δ 4.87 (m) | δ 1.98 (d, 8.8 Hz) | δ 7.66 (m) | δ 7.13 (m) | δ 4.6 (br, 1.5 PPM hwhh) |
| | | δ 5.77 (m) | δ 2.28 (d, 8.8 Hz) | δ 7.27 (m) | δ 7.00 (m) | |
| | | δ 5.78 (m) | $-\text{CO}-\text{CH}_2\text{R}$ | | δ 6.63 (m) | |
| | | δ 5.90 (m) | δ 3.08 (tod, $J_{\text{P}-\text{H}} = 29$ Hz, $J_{\text{H}-\text{H}} = 15$ Hz) | | | |
| | | | δ 3.52 (d, 15 Hz) | | | |
| 4 | n/a | δ 5.22 (br) | δ 1.74 (s) | δ 7.65 (m) | δ 7.11 (m) | δ -4.5 (br, 2 PPM hwhh) |
| | | δ 5.78 (br) | $-\text{CO}-\text{CH}_2\text{R}$ | δ 7.56 (m) | δ 6.85 (m) | |
| | | δ 5.93 (m) | δ 3.12 (tod, $J_{\text{P}-\text{H}} = 10$ Hz, $J_{\text{H}-\text{H}} = 14$ Hz) | δ 7.37 (m) | δ 6.52 (m) | |
| | | δ 6.01 (m) | | δ 7.24 (m) | | |
| | | | | | | |

the use of complexes like **B** for the preparation of functionalized alcohols is in progress.

4. Experimental

4.1. General considerations

Most of the compounds described were air sensitive and were prepared using either Schlenk or high-vacuum techniques. Solid compounds were manipulated in a Vacuum Atmospheres Corp. (VAC) HE-43 Dri-Lab with an HE-63P Pedatrol pressure regulator and HE-393 Dri Train. The inert gas used in the glovebox and Schlenk and vacuum lines was either nitrogen or argon, which was further purified by passage through activated Chemalog R3-11 catalyst and activated 4 Å molecular sieves. CO was CP grade and further dried by passage through a column of activated 4 Å molecular sieves. Solvents were all reagent grade and were further purified by standard techniques [22]. The complexes $(\eta^5\text{-C}_5\text{H}_4)\text{P}(\text{C}_6\text{H}_5)_2\text{ZrCl}_2$ and $(\eta^5\text{-C}_5\text{H}_4)\text{P}(\text{C}_6\text{H}_5)_2\text{ZrCl}_2$ [3,23] were prepared by literature methods.

4.2. Physical measurements

^1H and ^{31}P NMR spectra were obtained with Bruker AM-400 or AM-300 spectrometers. Proton NMR spectra were referenced by either the residual proton resonance or internal TMS; ^{31}P NMR spectra were referenced against external $\text{P}(\text{OCH}_3)_3$. Infrared spectra were obtained on a Perkin-Elmer Model 1600 series FTIR spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

4.3. $(\eta^5\text{-C}_5\text{H}_4)\text{P}(\text{C}_6\text{H}_5)_2(\eta^5\text{-C}_5\text{H}_5)\text{Zr}(\text{CH}_2\text{C}_6\text{H}_5)_2$ (**1**)

In the glove box, 4.00 g of $(\text{C}_5\text{H}_4)\text{P}(\text{C}_6\text{H}_5)_2(\text{C}_5\text{H}_5)\text{ZrCl}_2$ (8.4 mmol) and a magnetic stir bar were loaded in a 100 ml Schlenk flask. After transfer to a Schlenk line, 25 ml of ethyl ether was added and the suspension was stirred in an ice bath for about 10 min. Benzylmagnesium chloride in ether (18.0 ml 1.0 M (18.0 mmol)) was injected and the solution color changed from off-white to yellow-green over the course of an hour. The ice bath was removed the suspension warmed to room temperature and stirred for an additional 14 h. The ether was removed in vacuo, and the solid was dried under high vacuum for at least 18 h. The resulting yellow solid was extracted in a Soxhlet-type extractor with pentane for 72 h and the pentane was removed in vacuo. Two extractions were done to obtain a total of 4.93 g (94%) of **1**. NMR data. ^1H : C_5H_5 , δ 5.90 (s, 5 H), C_5H_4 , δ 6.03 (m, 2H), δ 6.07 (m, 2H), $\text{CH}_2\text{-Ph}$, δ

1.70 (d, $J = 10.8$ Hz, 2H), δ 1.67 (d, $J = 10.8$, 2H), $\text{P}(\text{C}_6\text{H}_5)_2$, δ 7.38 (m, 10 H), $\text{CH}_2\text{-C}_6\text{H}_5$, o - δ 6.69 (t, $J = 7.3$ Hz (2 H)), (p - δ 6.81 (t, $J = 7.3$ Hz (1 H)), m - δ 7.13 (t, $J = 7.3$ Hz (2 H)). ^{31}P : δ -19.13 (s) Analysis: calculated for $\text{C}_{36}\text{H}_{33}\text{PZr}$ (found): C, 73.56% (72.42%); H, 5.66% (5.86%) P, 5.27% (4.91%).

4.4. $(\eta^5\text{-C}_5\text{H}_4)\text{P}(\text{C}_6\text{H}_5)_2\text{Zr}(\text{CH}_2\text{C}_6\text{H}_5)_2$ (**2**)

A 100 ml Schlenk flask was loaded with 2.01 g (3.04 mmol) of $[\text{CpPPh}_2]_2\text{ZrCl}_2$ and a magnetic stirrer. Then 20 ml of freshly distilled ether was added under N_2 flush and 6.1 ml of 1 M benzyl magnesium chloride in ether (6.1 mmol) was added at room temperature in about 1 min. The suspension developed an orange color over the course of the addition. The flask was capped and stirred vigorously; an orange solution and a white precipitate developed in minutes. The suspension was stirred for 18 h, the solvent was removed in vacuo, and the resulting orange solid was dried for an additional 2 h. The orange solid was transferred to a Soxhlet-type extractor and 30 ml pentane was added. The solid was extracted with refluxing pentane for 60 h, the solvent was removed in vacuo, and the orange solid was dried for an additional 3 h to give 2.01 g of the crude product. The solid was then dissolved in 5 ml of boiling toluene and filtered into a Schlenk tube, layered with approximately an equal volume of pentane and left to mix at -10°C for 24 h. The supernatant was removed from the large, orange crystals which were washed twice with 5 ml pentane and the washings added to the supernatant. The crystals were washed once more with pentane and this colorless washing was discarded. The crystals were dried in vacuo for 10 h. A second crop was obtained from the combined supernatant and washing in a similar fashion gave a total of 1.90 g of **2** (81% based on the zirconocene dichloride). ^1H NMR (CD_2Cl_2): phenyl, δ 7.34 (m, 20 H); benzyl, m , δ 7.08 (t, $J_{\text{H-H}} = 7.7$ Hz, 4 H); p , δ 6.78 (t, $J_{\text{H-H}} = 7.4$ Hz, 2 H); o , δ 6.54 (dod, $J_{\text{H-H}} = 7.2$ Hz, $J_{\text{P-H}} = 0.91$ Hz, 4 H); C_5H_4 , (α), δ 6.02 (dod, $J_{\text{H-H}} = 2.5$ Hz, $J_{\text{P-H}} = 1.3$ Hz, 4 H); (β), δ 5.89 (t, $J_{\text{H-H}} = 2.5$ Hz, 4 H); $-\text{CH}_2-$, δ 1.48, (s, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): C_5H_4 , (β), δ 121.02 (s); (α) δ 119.86 (d, $J_{\text{P-C}} = 6.2$ Hz), P-C , 118.56 (d, $J_{\text{P-C}} = 12.3$ Hz); $\text{P-C}_6\text{H}_5$; *ipso*, δ 134.11 (d, $J_{\text{P-C}} = 21.3$ Hz); o , δ 138.21 (d, $J_{\text{P-C}} = 9.0$ Hz); m , δ 128.95 (d, $J_{\text{P-C}} = 8.0$ Hz); p , δ 129.54; $\text{CH}_2\text{-Ph}$, δ 63.44 (s); $-\text{CH}_2\text{-C}_6\text{H}_5$; p , δ 125.74; *ipso*, δ 153.16; m , δ 128.26; o , δ 116.67. $^{31}\text{P}\{^1\text{H}\}$ (CD_2Cl_2): δ -19.43. Analysis: calculated for $\text{C}_{48}\text{H}_{42}\text{P}_2\text{Zr}$ (found): C, 74.68% (73.70%); H, 5.48% (5.81%); P, 8.02% (7.85%).

4.5. Carbonylation of **1** and **2**

The preparation of **3** and **4** were accomplished by treatment of solutions of the parent complex in

dichloromethane with excess CO. In NMR experiments, typically a solution about 0.2 M of **1** or **2** (about 0.015 g in 0.8 ml) was frozen, the inert gas over the sample was removed by vacuum and CO was admitted at pressures from 0.3 to 0.7 atm. Isolation of the solid products was achieved by very similar means and a typical isolation is described below for complex **4**.

A 2.35 g sample of **2** was dissolved in 4 ml dichloromethane in one arm of an H-shaped crystallizer. The solution was filtered and then freeze-thaw degassed three times. CO (1 atm) was admitted and the solution thawed and warmed to ambient temperature and magnetically stirred for 30 min. Ether (4 ml) was transferred into the arm of the H-shaped crystallizer not containing the solution of **4**. The arm containing the solution of **4** was immersed in a NaCl–ice eutectic bath so that the ether slowly condensed onto the dichloromethane solution. After 48 h copious amounts of an orange precipitate were present under an orange solution. The apparatus was transferred to a -15°C freezer, allowed to cool to that temperature and then the supernatant was filtered off. The solid was washed twice with ether, the washings being combined with the supernatant in the H-shaped recrystallizer. The solvent was removed in vacuo to give an orange crystalline precipitate (1.02 g or 52%) and an orange oily residue from the combined washings and supernatant. It should be noted that the residue was composed of nearly all **4**. Also, in some instances, oils rather than crystals were obtained, but the oily material may be redissolved and treated as above to eventually give similar yields. See Tables 2 and 3 for NMR data. Analytical data. $(\eta^5\text{-C}_5\text{H}_4)\text{P}(\text{C}_6\text{H}_5)_2(\eta^5\text{-C}_5\text{H}_5)\text{Zr}(\text{CH}_2\text{C}_6\text{H}_5)(\text{-CO-CH}_2\text{C}_6\text{H}_5)$ (**3**), calculated for $\text{C}_{17}\text{H}_{13}\text{OPZr}$ (found): C, 72.16% (70.31%); H, 5.40% (5.37%); P, 5.03% (4.79%). $[(\eta^5\text{-C}_5\text{H}_4)\text{P}(\text{C}_6\text{H}_5)_2]_2\text{-ZrCH}_2\text{C}_6\text{H}_5(\text{-CO-CH}_2\text{C}_6\text{H}_5)$ (**4**), calculated for $\text{C}_{49}\text{H}_{42}\text{OP}_2\text{Zr}$ (found): C, 73.56% (71.81%); H, 5.29% (5.19%); P, 7.74% (7.27%).

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References

- [1] W. Tikkanen and J.W. Ziller, *Organometallics*, **10** (1991) 2266.
- [2] A.L. Kim, K.B. Lam, K. Ruekert and W. Tikkanen, *Organometallics*, **14** (1995) 1525.
- [3] C.P. Casey and F. Nief, *Organometallics*, **4** (1985) 1218.
- [4] P. Renaut, G. Tainturier and B. Gautheron, *J. Organomet. Chem.*, **148** (1978) 43.
- [5] W. Tikkanen, Y. Fujita and J.L. Petersen, *Organometallics* **5** (1986) 888.
- [6] W.R. Tikkanen and J.L. Petersen, *Organometallics*, **3** (1984) 1651.
- [7] P. Hofmann, P. Stauffert, K. Tatsumi, A. Nakamura and R. Hoffmann, *Organometallics*, **4** (1985) 404.
- [8] J.W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, **98** (1976) 1729.
- [9] K. Tatsumi, A. Nakamura, P. Hofmann, P. Stauffert and R. Hoffmann, *J. Am. Chem. Soc.*, **107** (1985) 4440.
- [10] G. Fachinetti, C. Floriani, F. Marchetti and S. Merlino, *J. Chem. Soc. Chem. Commun.*, (1976) 522.
- [11] G. Fachinetti, G. Fochi and C. Floriani, *J. Chem. Soc. Dalton Trans.*, (1977) 1946.
- [12] R.M. Waymouth, K.R. Clauser and R.H. Grubbs, *J. Am. Chem. Soc.*, **108** (1986) 6385.
- [13] S.A. Matchett, *Diss. Abstr. Int. B*, **47** (1986) 1984.
- [14] A.K. McMullen, I.P. Rothwell and J.C. Huffman, *J. Am. Chem. Soc.*, **107** (1985) 1072.
- [15] G. Erker and F. Rosenfeldt *J. Organomet. Chem.*, **188** (1980) C1.
- [16] M.F. Lappert, T.L.T. Ngoc and C.R.C. Milne, *J. Organomet. Chem.*, **174** (1979) C35.
- [17] A.S. Guram, Z. Guo and R.F. Jordan, *J. Am. Chem. Soc.*, **115** (1993) 4902.
- [18] A. Dormond and C. Moise *Polyhedron* **8** (1989) 2189.
- [19] R.M. Waymouth and R.H. Grubbs, *Organometallics*, **7** (1988) 1631.
- [20] J.M. Manriquez, D.R. McAlister, R.D. Sanner and J.E. Bercaw, *J. Am. Chem. Soc.*, **100** (1978) 2716.
- [21] P. Hofmann, P. Stauffert, M. Frede and K. Tatsumi, *Chem. Ber.*, **122** (1989) 1559.
- [22] A.J. Gordon and R.A. Ford, *The Chemist's Companion: A Handbook of Practical Data, Techniques and References*, Wiley, New York, 1972.
- [23] C.P. Casey, R.M. Bullock and F. Nief, *J. Am. Chem. Soc.*, **105** (1983) 7574.