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OXO-TITANIUM AND -ZIRCONIUM DIPHOSPHINES $[(\eta\text{-}C_5H_5)_2M(CH_2PPh_2)]_2O$ (WITH M = Ti, Zr) AS BUILDING BLOCKS FOR HETEROBIMETALLIC COMPLEXES

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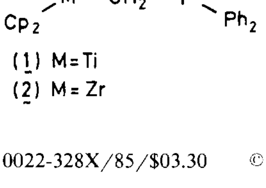
Summary

Oxo-titanium and -zirconium diphosphines $[(\eta\text{-}C_5H_5)_2M(CH_2PPh_2)]_2O$ (with M = Ti, Zr) were synthesized and treated with $[Rh(CO)_2Cl]_2$ to give the heterobimetallic d^0–d^8 species $O[(\eta\text{-}C_5H_5)_2M(CH_2PPh_2)]_2Rh(CO)Cl$.

Current interest in heterobimetallic complexes stems from their catalytic potential based on cooperativity action at the two metal centres; in this context the strong oxophilicity of titanium and zirconium can play a special role in CO activation [1,2]. Our recent finding that the hydroformylation catalytic activity of a rhodium(I) complex is enhanced by addition of the zirconium diphosphine $(\eta\text{-}C_5H_5)_2Zr(CH_2PPh_2)_2$ [3] prompted us to develop the synthesis of related derivatives in continuation of our investigations on the diphenylphosphinomethyl ligand in zirconium and titanium chemistry [4–7]. We report below the preparation and characterization of $[(\eta\text{-}C_5H_5)_2M(CH_2PPh_2)]_2O$ with M = Ti or Zr, diphosphines in which there are μ-oxo bonded two metal atoms involved in the five-membered chain between the two phosphorus atoms, and show that they can give heterobimetallic complexes, for example by reaction with $[Rh(CO)_2Cl]_2$.



(1) M = Ti
(2) M = Zr

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TABLE 1

^1H AND $^{31}P\{^1H\}$ NMR DATA FOR $[(\eta\text{-}C_5H_5)_2M(CH_2PPh_2)]_2O$ (M = Ti AND Zr) AND RELATED DERIVATIVES [a]

	^1H		$^{31}P\{^1H\}$
	δ(Cp)	$\delta(CH_2)$ (^2J(P–H))	δ(P)
(**1**)	6.25	2.25 (3.5)	2.7
$Cp_2TiCl(CH_2PPh_2)$ [b]	6.00	2.85 (3.5)	6.5
$Cp_2Ti(CH_2PPh_2)_2$ [b]	5.88	1.65 (3.5)	2.5
(**2**)	5.88	1.63 (2.4)	−4.3
$Cp_2ZrCl(CH_2PPh_2)$ [c]	5.81	1.84 (3.0)	2.5
$Cp_2Zr(CH_2PPh_2)_2$ [c]	5.76	0.97 (3.0)	−4.1

[a] Chemical shifts δ ppm and coupling constants (Hz) in parentheses; ^1H spectra in C_6D_6 solution; $^{31}P\{^1H\}$ spectra in THF/C_6D_6 solution (3/1 vol); values are positive downfield from external 85% H_3PO_4 in D_2O. [b] From ref. 7. [c] From ref. 8.

The derivatives $[(\eta\text{-}C_5H_5)_2Ti(CH_2PPh_2)]_2O$ (**1**) and $[(\eta\text{-}C_5H_5)_2Zr(CH_2PPh_2)]_2O$ (**2**) are obtained in ca. 50% yield when $LiCH_2PPh_2$. TMEDA (TMEDA = tetramethylethylene diamine) is allowed to react with $[(\eta\text{-}C_5H_5)_2TiCl]_2O$ or $[(\eta\text{-}C_5H_5)_2ZrCl]_2O$. Both **1** and **2** are air-sensitive microcrystalline solids, and have been characterized by analysis. The ^1H and $^{31}P\{^1H\}$ NMR data are in Table 1. From the ^{31}P chemical shifts, which do not differ greatly from those in related phosphinomethyl-titanium and -zirconium species, it can be assumed that there is no coordination of phosphorus to the metallic centre in **1** and **2**.

To investigate the ability of **1** and **2** to act as diphosphines towards late transition metals we treated them with $[Rh(CO)_2Cl]_2$. The heterometallic species $O[(\eta\text{-}C_5H_5)_2Ti(CH_2PPh_2)]_2Rh(CO)Cl$ (**3**) and $O[(\eta\text{-}C_5H_5)_2Zr(CH_2PPh_2)]_2Rh(CO)Cl$ (**4**) were readily obtained by precipitation from the reaction mixture, and the analyses were consistent with the suggested formula. The IR spectrum of each exhibits a strong ν(CO) band at 1950 cm^{-1}, but they are insufficiently soluble for reliable molecular weight determinations. The ^1H NMR spectrum of **4** shows a doublet of triplets for the methylene group, characteristic of a *trans* arrangement of two phosphorus nuclei bonded to rhodium(I) (^2J(P–H) + ^4J(P–H) = 2.7 Hz; ^3J(Rh–H) = 0.8 Hz), whereas in **3** only an unresolved broad peak is seen. The $^{31}P\{^1H\}$ spectra of **3** and **4** confirm phosphorus is coordinated to rhodium (I), with ^1J(P–Rh) in the range 116–122 Hz. For instance, for **3** there is a broad doublet at δ 37.6 ppm, ^1J(P–Rh) 116 Hz, closely similar to the data for the predominant isomer of $[(C_5H_5)_2Ti(CH_2PPh_2)_2Rh(CO)Cl]_2$ (Table 2). In the case of the zirconium analogue **4** the existence of slowly exchanging rotamers is deduced from ^{31}P NMR spectra, which show a predominant ABX pattern accompanied by several less intense A_2X resonances. This indicates that the main isomer has two non equivalent phosphorus nuclei in *trans* position to the rhodium, while in the minor isomers the two phosphorus are equivalent. Such a mixture of ABX and A_2X patterns, indicating the presence of stereorigid conformers involved in slow intramolecular exchange at room temperature, has been previously observed for related systems such as for the monomeric **6** [1] and the dimeric **5** [7], and arises from the different mutual arrangements of the phenyl groups bonded to the two phosphorus *trans*-coordinated to rhodium.

TABLE 2

^{1}H AND ^{31}P{^{1}H} NMR DATA FOR O[(η-C_5H_5)$_2$M(CH_2PPh_2)]$_2$Rh(CO)Cl (M = Ti AND Zr) AND RELATED DERIVATIVES [a]

	^{1}H		^{31}P{^{1}H}		
	δ(Cp)	δ(CH_2)(^2J(P-H)+^4J(P-H))	δ(^{31}P)	(J(RhP))	(J(P-P))
(3)	6.06 [b]	2.93 [b]	37.6	(116)	
[$Cp_2Ti(CH_2PPh_2)_2Rh(CO)Cl]_2$ [g]	6.11	2.18 (3.0)	36.2 [c]	(117)	
(5)			14.9	(118)	
			[d] 36.5	(120)	(322)
			14.6	(120)	(322)
(4)	6.33 [e]	2.13 [f] (2.7)	[c, d, e] 37.6	(119)	(360)
			15.3	(122)	(360)
$Cp_2Zr(CH_2PPh_2)_2Rh(CO)Cl$ [g]	6.10	2.16 [f] (3.4)	[d] 37.4	(120)	(316)
(6)			24.0	(136)	(316)
$Cp_2ZrCl(CH_2PPh_2)_2Rh(CO)Cl$ [g]	5.98	2.16 [f] (3.4)	[d] 34.3	(120)	(363)
(7)			13.8	(120)	(363)
			34.5	(117)	
			13.0	(117)	

[a] Chemical shifts δ ppm and coupling constants (Hz) in parentheses, ^{1}H spectra in C_6D_6 solution; ^{31}P{^{1}H} in THF/C_6D_6 solution (3/1 vol), values are positive downfield from external 85% H_3PO_4 in D_2O. [b] Broad singlet. [c] Main rotamer at room temperature. [d] ABX pattern. [e] Other minor peaks: ^{1}H, Cp at 6.28, 6.25, 6.19, 6.15 ppm; ^{31}P{^{1}H}, doublets at 36.56 (118); 36.32 (118); 35.90 (119); 35.41 (116) ppm (Hz). [f] J(Rh-H): 0.8 Hz in **4**; 0.9 Hz in **6** and 1.2 Hz in **7**. [g] Literature data: **5** from ref. 7; **6** from ref. 1 and **7** from ref. 5.

Experimental

All preparations were carried out under argon using Schlenk techniques.

Preparation of [$Cp_2Ti(CH_2PPh_2)]_2O$ (1)

A solution of $LiCH_2PPh_2$,TMEDA (11.7 g, 36.0 mmol) in THF (20 ml) was added dropwise at −78°C to a solution of $(Cp_2TiCl)_2O$ (8.0 g, 18.0 mmol) in THF (50 ml). The deep yellow solution was allowed to come to room temperature after which the solvent was concentrated to 5 ml and pentane was added to precipitate a solid. This was filtered off, washed twice with pentane (2 × 20 ml), and dissolved in 60 ml toluene to remove LiCl. After filtration through Celite, the deep yellow solution was concentrated and a layer of pentane was placed on it. Diffusional mixing of the solvent gave a microcrystalline yellow product, which was filtered off, washed with pentane, and dried under vacuum.

Analysis. Found: C, 70.1; H, 5.7; Ti, 12.6. $C_{46}H_{44}OP_2Ti_2$ calcd.: C, 71.7; H, 5.7; Ti, 12.4%.

Preparation of [$Cp_2Zr(CH_2PPh_2)]_2O$ (2)

The reaction was carried out at room temperature following the procedure described above, to give a white microcrystalline product.

Analysis. Found: C, 64.4; H, 5.2; Zr, 21.4. $C_{46}H_{44}OP_2Zr_2$ calcd.: C, 64.4; H, 5.1; Zr, 21.3%.

Preparation of O[$Cp_2Ti(CH_2PPh_2)]_2Rh(CO)Cl$ (3)

A solution of $[(Rh(CO)_2Cl)]_2$ (0.150 g, 0.38 mmol) in 20 ml THF was added dropwise at room temperature to a THF solution of **1** (0.595 g; 0.77 mmol) and the evolved CO was pumped off continuously during the reaction. The solution was concentrated after 1 h stirring and pentane added to give a yellow precipitate **3**, which was filtered off.

Analysis. Found: C, 58.6; H, 4.7: Ti, 10.8; P, 6.6. $C_{47}H_{44}O_2P_2ClTi_2Rh$ calcd.: C, 60.2; H, 4.7; Cl, 3.8; Ti, 10.2; P, 6.6%.

*Preparation of [O(Cp$_2$Zr(CH$_2$PPh$_2$)]$_2$Rh(CO)Cl (**4**)*

A similar procedure was used, and precipitation of **4** occurred immediately after complete addition.

Analysis. Found: C, 54.6; H, 4.4.; Cl, 3.6; Zr, 17.8. $C_{47}H_{44}O_2P_2ClZr_2Rh$ calcd.: C, 55.5; H, 4.4; Cl, 3.5; Zr, 17.8%.

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