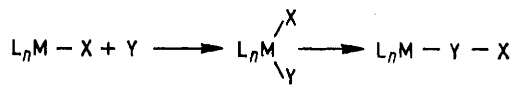
Carbon Monoxide Insertion into Zirconium– and Hafnium–Carbon σ-Bonds: Synthesis, and Structural and Thermodynamic Data for Alkyl- and Aryl-η-acylbis(η-cyclopentadienyl)derivatives of Zirconium(IV) and Hafnium(IV) [1]

By **Giuseppe Fachinetti, Giovanni Fochi, and Carlo Floriani,*** Istituto di Chimica Generale, Università di Pisa, 56100 Pisa, Italy

Carbonylation of toluene solutions of bis(η-cyclopentadientyl)diphenyl-zirconium(IV) and -hafnium(IV), $[M(cp)_2(Ph)_2]$ (cp = η-C_5H_5; M = Zr or Hf), with CO at atmospheric pressure gave acyl derivatives $[M(cp)_2(COPh)(Ph)]$ [ν(CO) = 1 500 cm^{-1}]. The same results were obtained for $[M(cp)_2R_2]$ (M = Zr or Hf; R = CH_2Ph or Me), but in these cases the carbonyl insertion was found to be reversible. The isolation of $[M(cp)_2(COR)R]$ [ν(CO) = 1 530—1 550 cm^{-1}] was possible only for zirconium, while under the same conditions equilibrium constants and thermodynamic data were obtained for CO insertion into the Hf–Me ($\Delta H^{\ominus} = -12.7 \pm 1.6$ kcal mol^{-1}; $\Delta S^{\ominus} = -33.0 \pm 5.6$ cal K^{-1} mol^{-1}) and Hf–CH_2Ph ($\Delta H^{\ominus} = -11.5 \pm 0.2$ kcal mol^{-1}; $\Delta S^{\ominus} = -28.7 \pm 0.6$ cal K^{-1} mol^{-1}) bonds. All the acyls show a low CO stretching frequency, which indicates an η-acyl bonded group, as was confirmed by *X*-ray structural data.

IN spite of the wide interest in insertion reactions, a synthetic approach to the general aspects of this type of reactions is frequently ignored.[2] We reported recently a chemical study on bis(η-cyclopentadienyl)vanadium(III) derivatives, whose reactivity pattern can be used to correlate, in some way, the nature of the inserting (Y) and the migrating (X) group:[3]



$$L_nM-X+Y \longrightarrow L_nM\genfrac{}{}{0pt}{}{/X}{\backslash Y} \longrightarrow L_nM-Y-X$$

Complexes like $[Ti(cp)_2R(X)]$[4] (X = halogen, cp = η^5-cyclopentadienyl) or $[V(cp)_2X]$ (X = halogen, alkyl, aryl, or SR) are suitable models from both steric and electronic points of view, as they have an open shell configuration (16 electrons) together with the steric requirements for the proximity between the inserting and the migrating groups.

In the reaction of carbon monoxide only one potentially migrating group is present on the metal for both types of complexes. The present report on the carbonylation of dialkyl- and diphenyl-bis(η-cyclopentadienyl) derivatives of zirconium(IV) and hafnium(IV) gives insight in the case of more than one alkyl or aryl group bonded to the same metal. The comparison between the reported results and those obtained for analogous derivatives of titanium allows us to rationalise the observed trend in the CO insertion into metal–carbon σ bonds.

EXPERIMENTAL

Unless otherwise stated, all the reactions described here were carried out under an atmosphere of purified nitrogen or carbon monoxide; solvents were purified by standard methods. I.r. spectra were measured with a Perkin-Elmer 337 spectrometer and n.m.r. spectra with a T-60 Varian spectrometer. Equilibrium data were measured gas-volumetrically using previously described equipment.[5] The concentration of CO in toluene was determined experimentally from 286 to 314 K and extrapolated to the other temperatures.[6] The absorption of CO was carried out in toluene as solvent at the total (CO + vapour of the solvent) constant pressure of 1 atm.†

Some of the typical reactions are described in detail, the preparation of the other complexes being carried out under similar conditions. Dimethyl- and diphenyl-bis(η-cyclopentadienyl)-zirconium(IV) and -hafnium(IV) were prepared as previously described.[7]

Preparations.—Dibenzylbis(η*-cyclopentadienyl*)*hafnium*(IV). The compound $[Hf(cp)_2Cl_2]$ (10 g, 26.3 mmol) was suspended in diethyl ether and cooled to −50 °C. An ether solution of $PhCH_2MgCl$ (70 cm^3, 0.76 mol dm^{-3}) was added dropwise with stirring. At the end of the addition the yellow suspension was kept at room temperature and stirred for 12 h. The solvent was completely evaporated and the residue extracted with toluene (150 cm^3). After filtration a yellow solution was obtained which was concentrated to 30 cm^3. On addition of heptane, $[Hf(cp)_2(CH_2Ph)_2]$ was obtained as a yellow crystalline solid, which was recrystallised from toluene–heptane (*ca.* 80%).

Acetylbis(η*-cyclopentadienyl*)*methylzirconium*(IV). A toluene solution (20 cm^3) of $[Zr(cp)_2Me_2]$ (10 g, 39.8 mmol) was treated with purified carbon monoxide at atmospheric

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† 1 atm = 101 325 Pa.

[1] Part of this work has been briefly communicated: G. Facinetti, C. Floriani, F. Marchetti, and S. Merlino, *J.C.S. Chem. Comm.*, 1976, 522.

[2] A. Woijcicki, *Adv. Organometallic Chem.*, 1973, **11**, 87; 1974, **12**, 31.

[3] G. Fachinetti, S. Del Nero, and C. Floriani, *J.C.S. Dalton*, 1976, 203.

[4] G. Fachinetti and C. Floriani, *J. Organometallic Chem.*, 1974, **71**, C5.

[5] F. Calderazzo and F. A. Cotton, *Inorg. Chem.*, 1962, **1**, 30.

[6] F. Calderazzo, G. Fachinetti, and C. Floriani, *J. Amer. Chem. Soc.*, 1974, **96**, 3695.

[7] E. Samuel and M. D. Rausch, *J. Amer. Chem. Soc.*, 1973, **95**, 6263.

pressure and room temperature. A fast absorption of CO was followed by a slight change in the colour of the solution. On addition of heptane (100 cm^3), under CO atmosphere, and cooling to −80 °C, light yellow crystals of [Zr(cp)$_2$(COMe)Me] were obtained (*ca.* 80%). Absorption measurements in toluene gave CO : Zr = 0.95 : 1 at 290 K.

Benzylbis(η-cyclopentadienyl)(phenylacetyl)zirconium(IV). A toluene solution (30 cm^3) of [Zr(cp)$_2$(CH$_2$Ph)$_2$] (1.6 g, 4.0 mmol) was treated with purified carbon monoxide at atmospheric pressure and room temperature for 1 h. On addition of heptane (100 cm^3), under CO atmosphere, and cooling to −80 °C, light yellow crystals of [Zr(cp)$_2$(COCH$_2$Ph)(CH$_2$Ph)] were obtained (*ca.* 80%). Absorption measurements of CO in toluene solution gave CO : Zr = 0.92 : 1 at 290 K.

(Benzoyl)bis(η-cyclopentadienyl)phenylzirconium(IV). A toluene solution (50 cm^3) of [Zr(cp)$_2$Ph$_2$] (3.02 g, 8.05 mmol) was treated with purified carbon monoxide at atmospheric pressure for 1 h. The solution rapidly absorbed CO and at once became orange. The concentrated solution (25 cm^3) was treated with heptane (100 cm^3) and cooled to −80 °C gave yellow-orange crystals of [Zr(cp)$_2$(COPh)Ph] (*ca.* 80%), m.p. 23 °C. Absorption measurements of CO in toluene gave CO : Zr = 0.95 : 1 at 295 K.

TABLE 1

Analytical data for the complexes

Complex	Colour	Analysis [a] (%) C	H	M [a,b]	Yield (%)	CO/metal [c] [T/K]
[Zr(cp)$_2$(CH$_2$Ph)$_2$]	Yellow	72.2 (71.5)	5.9 (6.0)	390 (403)	45	
[Zr(cp)$_2$(COMe)Me]	Light yellow	55.8 (55.9)	5.7 (5.7)	264 (279)	80	0.95 [290]
[Zr(cp)$_2$(COCH$_2$Ph)(CH$_2$Ph)]	Light yellow	69.8 (69.6)	5.9 (5.6)	448 (431)	80	0.92 [290]
[Zr(cp)$_2$(COPh)Ph]	Yellow-orange	68.5 (68.5)	5.3 (5.0)	370 (403)	80	0.95 [295]
[Hf(cp)$_2$(CH$_2$Ph)$_2$]	Yellow	59.2 (58.7)	5.3 (4.9)		80	
[Hf(cp)$_2$(COPh)Ph]	Yellow-orange	56.4 (56.3)	4.2 (4.1)	428 (490)	72	0.97 [295]

[a] Calculated values given in parentheses. [b] By cryoscopy in benzene. [c] Molar value CO/metal determined by gas-volumetric absorption measurements carried out in toluene.

(Benzoyl)bis(η-cyclopentadienyl)phenylhafnium(IV). A toluene solution (10 cm^3) of [Hf(cp)$_2$Ph$_2$] (1.45 g, 8.1 mmol) was treated with purified CO at atmospheric pressure and room temperature for 4 h. The colour of the solution became immediately orange. On addition of pentane (50 cm^3) and cooling to −80 °C, yellow-orange crystals of [Hf(cp)$_2$(COPh)Ph] were obtained (*ca.* 72%), m.p. 22 °C. Absorption measurements of CO in toluene gave CO : Hf 0.97 : 1 at 295 K.

RESULTS AND DISCUSSION

The reactions of [M(cp)$_2$R$_2$] (cp = η-C$_5$H$_5$; M = Zr or Hf; R = CH$_2$Ph, Me, or Ph),[7] with carbon monoxide are strongly dependent on both the metal and the nature of the alkyl group. These results are summarised in equations (1) and (2), and may be compared with those obtained for titanium in equation (3).[8]

Complexes (1), dissolved in toluene, absorbed CO reversibly at atmospheric pressure and room temperature. The equilibrium depicted in (1) is completely shifted to the right for zirconium at 20 °C, while the carbonylation is incomplete for hafnium derivatives, as is shown by gas-volumetric absorption measurements. The isolation of (2) is possible only for zironium, all the operations being carried out under a CO atmosphere. The compounds [Zr(cp)$_2$(COR)R] (R = CH$_2$Ph or Me) are stable against release of CO in the solid state, but when dissolved in toluene they are reconverted *in vacuo* into the starting compounds. The n.m.r. spectra measured during and at the end of the carbonylation show clearly, in each case, that the species involved in reaction (1) are the starting dialkyls (1) and the acyl–alkyl derivatives (2). Reversible absorption and release of CO can be followed *via* n.m.r. spectroscopy. These results rule out both the possible formation of diacyl species and the further reaction of (2) to give other products.

$$\underset{(1)}{[\mathrm{M(cp)_2R_2}]} + \mathrm{CO} \overset{\text{toluene}}{\rightleftharpoons} \underset{(2)}{[\mathrm{M(cp)_2(COR)R}]} \qquad (1)$$

$$\mathrm{M = Zr\ or\ Hf;\ R = CH_2Ph\ or\ Me}$$

$$\underset{(3)}{[\mathrm{M(cp)_2Ph_2}]} + \mathrm{CO} \xrightarrow{\text{toluene}} \underset{(4)}{[\mathrm{M(cp)_2(COPh)Ph}]} \qquad (2)$$

$$\mathrm{M = Zr\ or\ Hf}$$

$$[\mathrm{Ti(cp)_2(CH_2Ph)_2}] + 3\,\mathrm{CO} \xrightarrow{\text{heptane}} [\mathrm{Ti(cp)_2(CO)_2}] + \mathrm{(PhCH_2)_2CO} \qquad (3)$$

The diphenyl derivatives (3) absorb one mol of CO per metal atom, which is not released *in vacuo*, either in the solid state or in solution. There is considerable difference between titanium and hafnium or zirconium. As previously suggested[4,8] the synthesis of a titanium(II) carbonyl [equation (3)] can be interpreted *via* the intermediate formation of an alkyl–acyl species such as (2) or (4). The same results have been obtained in the carbonylation of [Ti(cp)$_2$Ph$_2$].[9]

The elimination of two groups from the same metal atom is typical behaviour in organotitanium chemistry.[10]

The formulation of (2) and (4) as acyl–alkyl derivatives can be justified on the basis of the analytical results, CO absorption measurements, and spectroscopic data (Tables 1 and 2). We will point out some general properties of (2) and (4), *e.g.* the unusual low stretching frequency of the acyl group (Table 2) and the unreactivity of (2) and (4) towards either reductive elimination, as was found for titanium,[4,8,9] or further carbonylation of

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[8] G. Fachinetti and C. Floriani, *J.C.S. Chem. Comm.*, 1972, 654.

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TABLE 2

Hydrogen-1 n.m.r. and i.r. spectroscopic data

Complex	Chemical shift (τ) (in C_6D_6)	Relative intensity (nH)	Assignment	I.r. ν(CO) acyl (cm^{-1})
$[Zr(cp)_2(CH_2Ph)_2]$	8.16 (s)	4	CH_2	
	4.54 (s)	10	η-C_5H_5	
	3.33—2.65 (m)	10	Ph	
$[Zr(cp)_2(COMe)Me]$	9.55 (s)	3	Me	1 545 [a]
	7.59 (s)	3	Me	1 540 [b]
	4.65 (s)	10	η-C_5H_5	
$[Zr(cp)_2(COCH_2Ph)(CH_2Ph)]$	7.42 (s)	2	CH_2	1 540 [a]
	6.25 (s)	2	CH_2	
	4.86 (s)	10	η-C_5H_5	
	2.88 (bm)	10	Ph	
$[Zr(cp)_2(COPh)Ph]$	4.55 (s)	10	η-C_5H_5	1 510 [c]
	2.63 (m, br)	6	Ph	
	2.03 (m, br)	2	Ph	
	1.62 (m, br)	2	Ph	
$[Hf(cp)_2(COMe)Me]$	10.31 (s) [10.25 (s)] [d]			1 550 [b]
	9.60 (s)	3	Me	
	7.60 (s)	3	Me	
	4.73 (s)	10	η-C_5H_5	
	4.35 (s) [4.30 (s)] [d]			
$[Hf(cp)_2(COCH_2Ph)(CH_2Ph)]$	8.50 (s) [8.45 (s)] [d]			
	7.65 (s)	2	CH_2	1 530 [b]
	6.27 (s)	2	CH_2	
	4.92 (s)	10	η-C_5H_5	
	4.53 (s) [4.51 (s)] [d]			
	2.91 (m, br)			
$[Hf(cp)_2(COPh)Ph]$	4.62 (s)	10	η-C_5H_5	1 500 [c]
	2.63 (bm)	6	Ph	
	2.02 (bm)	2	Ph	
	1.55 (m)	2	Ph	
$[Hf(cp)_2(CH_2Ph)_2]$	8.45 (s)	4	CH_2	
	4.51 (s)	10	η-C_5H_5	
	2.94 (bm)	10	Ph	

[a] In Nujol. [b] In CH_2Cl_2 solution. [c] Neat liquid. [d] Values corresponding to unreacted starting compounds, whose chemical shifts are reported in brackets.

the second alkyl group. Finally the observed trend in the insertion of CO into the metal–carbon σ-bond as a function of the nature of the metal and the alkyl group will be justified.

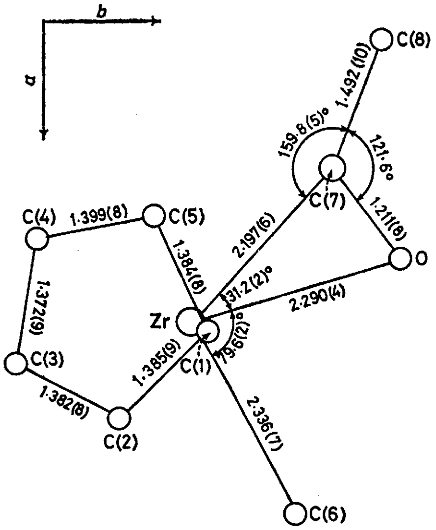

FIGURE 1 A view of the complex $[Zr(cp)_2(COMe)Me]$ along the c axis

An explanation for some of these results can be found in the structure of $[Zr(cp)_2(COMe)Me]$,[1,11] which deserves some discussion. A view of the complex is shown in Figure 1. Relevant bond distances and bond angles are given in Table 3. Zirconium is η-bonded to two bent cyclopentadienyl rings. The molecule has C_s symmetry, and the mirror plane through Zr contains the acetyl and the methyl groups. The marked deviation from the sp^2 bond angles around C(7), as well as the Zr–O [12] bond distance, show that the acyl unit is η–CO-bonded to the

TABLE 3

Some relevant bond distances (Å) and bond angles (°) with estimated standard deviations. (The atom numbering is shown in Figure 1)

Zr–C(1)	2.520(5)	C(5)–C(1)–C(2)	106.4(5)
Zr–C(2)	2.526(6)	C(1)–C(2)–C(3)	109.7(5)
Zr–C(3)	2.506(5)	C(2)–C(3)–C(4)	107.4(5)
Zr–C(4)	2.494(5)	C(3)–C(4)–C(5)	107.9(5)
Zr–C(5)	2.507(6)	C(4)–C(5)–C(1)	108.6(5)
Zr–C (av.)	2.511	C(6)–Zr–O	79.6(2)
C(1)–C(2)	1.385(9)	O–Zr–C(7)	31.2(2)
C(2)–C(3)	1.382(8)	C(6)–Zr–C(7)	110.8(2)
C(3)–C(4)	1.372(9)	O–C(7)–C(8)	121.6(6)
C(4)–C(5)	1.399(8)	Zr–C(7)–C(8)	159.8(5)
C(5)–C(1)	1.384(8)	Zr–C(7)–O	78.6(4)
C–C (av.)	1.384	cp–Zr–cp	129.8(4)
Zr–C(6)	2.336(7)		
Zr–C(7)	2.197(6)		
Zr–O	2.290(4)		
O–C(7)	1.211(8)		
C(7)–C(8)	1.492(10)		
cp(⊥)–Zr	2.217		

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[11] F. Marchetti and S. Merlino, unpublished work.

[12] V. W. Day and R. C. Fay, *J. Amer. Chem. Soc.*, 1975, **97**, 5136, and refs. therein.

metal. The acetyl group acts in this case as a bidentate three-electron donor.

This η-bonding picture for the acyl group finds further support in the shortening of the Zr–C(7) distance, which is reminiscent of the metal–C(carbene) interaction, and in the lengthening of the C–O ketonic bond distance.[13] It is evident that in [Zr(cp)$_2$(COMe)Me], the acyl group closely resembles the ethylene ligand in [Nb(cp)$_2$(Et)(C$_2$H$_4$)].[14]

The interaction reported between the metal and the acyl group explains the unusual lowering of the CO stretching frequency (Table 2). Such a low frequency is normally found for early transition metals in high oxidation states and with an open shell configuration {[Zr(cp)$_2$(COR)Cl],[15] ν(CO) 1 550 cm^{-1}; [Ti(cp)$_2$(COR)X],[4] ν(CO) 1 625—1 603 cm^{-1}}. With the same mechanism the acyl ligand can stabilise, acting as an η-bonded ligand, some co-ordinatively and electronically unsaturated intermediates formed during the CO insertion into the metal–carbon σ bond.[2] The difference in the CO-(acyl) stretching frequency between (2) and (4) can be explained by a higher stabilisation of the η-bonded form for the acyl group when a phenyl substituent is present. This, moreover, is in agreement with the observed higher relative stability of the benzoyl compared to the phenyl form [equation (2)].

Since the metal–acyl derivatives are intermediates in many catalytic processes,[2] the knowledge of the metal–acyl bonding model becomes especially important. Three different classes of metal–acyl derivatives can be recognised: (*a*) *C*-bonded σ-acyls; [16,17] (*b*) *C*- and *O*-bonded μ-acyls, bridging two metal centres; [18] and (*c*) η-acyls, *C*- and *O*-bonded to the same metal.[19]

It was recently observed that a feature of insertion reactions is that, when more than one metal–carbon σ-bonded group is present, not all the groups react with the inserting reagents.[20] We did not observe further insertion of CO into metal-alkyl bonds in (2) and (4), as might be expected on the basis of the reported structure. The carbon monoxide insertion for complexes like [Ti(cp)$_2$(R)X],[4] [V(cp)$_2$X],[3] (1) and (2), can be depicted as passing through a co-ordination of CO to the 16-electron-species:

insertion process. The presence of the η-form for the acyl group even in solution can be deduced from the i.r. spectrum of (2) and (4) in CH$_2$Cl$_2$ showing the CO acyl band at almost the same frequency.

The results of the carbonylation of [Ti(cp)$_2$(CH$_2$Ph)$_2$] might suggest the evolution of (2) and (4) towards a ketone elimination and the formation of a zirconium(II) species. The structure of [Zr(cp)$_2$(COMe)Me] shows that the migration of the nucleophile-like C(6) to the suspected electrophilic C(7) is prevented by the presence of the coplanar acyl oxygen between the two carbon atoms. The abnormal Zr–C(6) bond distance, if compared with reported values,[21] seems to indicate a labilising effect being induced by the co-ordination of the acyl oxygen on the zirconium–methyl bond. This might be an interesting result in suggesting a metal–ligand lengthening (labilisation), as depending on the number of metal valence electrons in the [M(cp)$_2$L$_n$] class of complexes. The function of CO in reactions like (4) can be recognised both through a labilising effect on the M–C σ bond and in providing a ' compatible ' inserting group for a migrating alkyl unit.[3]

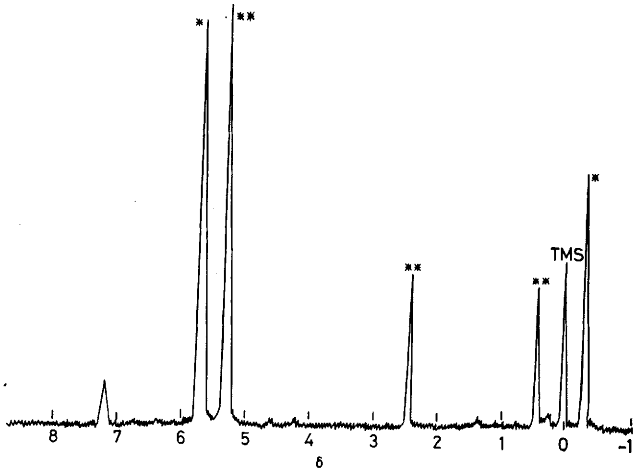
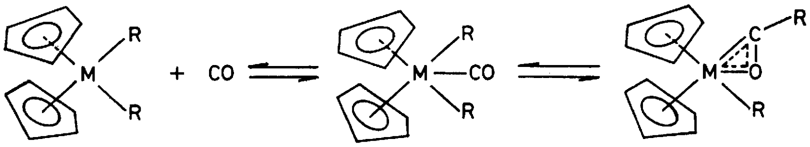


FIGURE 2 N.m.r. spectrum for the reaction [Hf(cp)$_2$Me$_2$] + CO $\rightleftharpoons$ [Hf(cp)$_2$(COMe)Me]. Peaks marked * are due to starting material, peaks marked ** are due to product



(4)

The co-ordination of the acyl oxygen on zirconium in (2) and (4) prevents a further CO addition for the second

Equilibrium Studies.—As can be checked by the n.m.r. spectrum (Figure 2), the reaction of [Hf(cp)$_2$R$_2$] (R = CH$_2$Ph or Me) with CO gives only the mono-insertion product without any by-products or further reaction of the

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[13] F. A. Cotton, B. A. Frenz, and A. Shaver, *Inorg. Chim. Acta*, 1973, **7**, 161.

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[17] M. R. Churchill and S. W. Y. Chang, *Inorg. Chem.*, 1975, **14**, 1680; M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, 1968, **7**, 953.

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[21] L. Atwood, W. E. Hunter, D. C. Hrncir, E. Samuel, H. Alt, and M. D. Rausch, *Inorg. Chem.*, 1975, **14**, 1757.

resulting stable alkyl–acyl derivatives, $[Hf(cp)_2(COR)R]$. The equilibrium depicted in equation (1) is rapidly established (<1 h). This enables us to determine the equilibrium constants and thermodynamic parameters for CO insertion into Hf–C σ bonds. Equilibrium constants for $[Hf(cp)_2R_2]$ were gas-volumetrically measured at temperatures between 268.6 and 307.2 K in toluene solutions. The results are reported in Table 4, together with the corresponding thermodynamic values.

In order to discern a regular trend of the reported results for the CO-insertion reaction, based on the nature of the metal and the alkyl groups, equations (1)—(3) must also be considered. The observed difference between titanium, zirconium, and hafnium can be ascribed to an increasing metal–alkyl *vs.* metal–acyl bond strength. The order of the metal–carbon bond strength, Ti $\ll$ Zr < Hf, was observed for some MR_4 derivatives (M = Ti, Zr, or Hf; R = Me_3SiCH_2, Me_3CCH_2, or $PhCH_2$),[22] and this trend appears to apply to other groups.[23]

TABLE 4

Equilibrium data for the reaction [a] $[Hf(cp)_2R_2] + CO \overset{\text{toluene}}{\rightleftharpoons} [Hf(cp)_2(COR)R]$

R	T/K	10^3[CO] [b]/ mol dm^{-3}	$10^{-2}K$/ dm^3 mol^{-1}	Thermodynamic parameters
CH_2Ph	268.6	7.22	12.58	$\Delta H^\ominus = -11.5 \pm 0.2$ kcal mol^{-1}
	277.5	7.35	6.33	$\Delta S^\ominus = -28.7 \pm 0.6$ cal K^{-1} mol^{-1}
	288.4	7.42	2.82	
	297.4	7.47	1.56	
	307.2	7.42	0.84	
Me	269.6	7.24	15.03	$\Delta H^\ominus = -12.7 \pm 1.6$ kcal mol^{-1}
	277.3	7.35	6.47	$\Delta S^\ominus = -33.0 \pm 5.6$ cal K^{-1} mol^{-1}
	288.5	7.42	2.56	
	297.4	7.47	1.49	
	307.2	7.42	0.78	

[a] 1 atm constant pressure (CO + solvent vapour pressure). [b] Concentration of CO in toluene experimentally determined.

The higher stability of the acyl form for the phenyl derivatives, $[M(cp)_2(COPh)Ph]$ (M = Zr or Hf), compared to the other acyls can be related not to a decreasing M–phenyl *vs.* M–alkyl bond strength, but rather to an increased M–acyl interaction due to the presence of the phenyl substituent.

The dissociation energies for the Ti–Me (60 kcal mol^{-1}) and Ti–Ph (84 kcal mol^{-1}) bonds in the corresponding $[Ti(cp)_2R_2]$ (R = Me or Ph) have been determined.[24] In this connexion we must consider the resemblance between the thermodynamic values reported for the carbonylation of $[Hf(cp_2)R_2]$ (R = Me or CH_2Ph). These similar features do not entail similar Hf–Me and Hf–CH_2Ph bond strengths. More probably the factor overcoming all the other effects, thus making equal the thermodynamic parameters for the two alkyls, is the η-bonded interaction of the acyl with the metal.

In spite of the very wide exploration on insertion reactions, very few thermodynamic data seem available for other systems.[2] A regular trend in the equilibrium constants was observed for CO insertion in $[MnR(CO)_5]$ [25] and $[RhR(CO)(PPh_3)_2Cl_2]$.[2,26] The equilibrium constant increases in the order $PhCH_2$ < Ph < Me < Et, presumably as a result of the relative metal–carbon bond strength. In these cases, contrary to our findings, the factor which determines the relative stabilities of the acyls and the corresponding alkyls is not the acyl–metal interaction, but rather the metal–carbon bond strength of the starting alkyl.

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