Journal of Organometallic Chemistry, 272 (1984) C37—C39
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

HIGH YIELD SYNTHESES AND CHARACTERISATION OF A NEW ZIRCONOCENE(II) DICARBONYL $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\}_2(CO)_2]$, A CONVENIENT PRECURSOR TO VARIOUS ZIRCONOCENE(II or IV) COMPLEXES*

ANTONIO ANTIÑOLO, MICHAEL F. LAPPERT, and DUNCAN J.W. WINTERBORN
School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)

(Received June 13th, 1984)

Summary

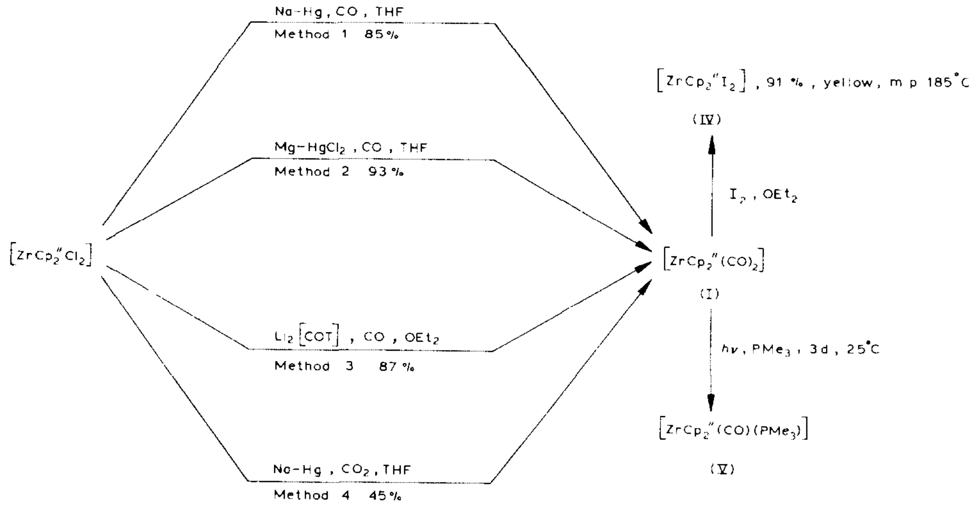
The dark green crystalline $[ZrCp''_2(CO)_2]$ ($Cp'' = \eta\text{-}C_5H_3(SiMe_3)_2$), (I) ($\delta$(^{13}CO) 264 ppm), was prepared by reduction from $[ZrCp''_2Cl_2]$ and either CO (using Na—Hg, Mg—$HgCl_2$, or Li_2[COT]) or CO_2(Na—Hg) in high (CO) to moderate (CO_2) yield; the Na—Hg/CO procedure was much more effective than for Zr analogues having $\eta\text{-}\overline{C}_5H_5$ or $\eta\text{-}\overline{C}_5H_4(SiMe_3)$ ligands; the carbonyl complex I is a convenient precursor to CO-free derivatives obtained either by oxidative addition or ligand displacement.

The only stable carbonyls of zirconium and hafnium (M) at present known are the metallocene(II) complexes $[MCp_2(CO)_2]$ ($Cp = \eta\text{-}C_5H_5$) and $[MCp^{\star}_2(CO)_2]$ ($Cp^{\star} = \eta\text{-}C_5Me_5$) [1], as well as $[MCp_2(CO)L]$ (e.g. L = PMe_3) [2]. In view of our interest in the lipophilic, bulky trimethylsilylcyclopentadienyl ligands $\eta\text{-}\overline{C}_5H_3(SiMe_3)_2$ (abbreviated as $\overline{Cp}''$) and, to a lesser extent, $\eta\text{-}\overline{C}_5H_4(SiMe_3)$ ($\overline{Cp}'$) to stabilise unusual complexes (e.g., the metallocene(III) chlorides of early (f^0—f^3) lanthanoids, $[(LnCp''_2Cl)_2]$, for which corresponding $\overline{Cp}$, $\overline{Cp}'$, or $\overline{Cp}^{\star}$ complexes are not accessible [3]), we sought to examine $[MCp''_2(CO)_2]$ and $[MCp'_2(CO)_2]$.

We now present our preliminary findings, which demonstrate: (i) high yield syntheses (methods 1—3, Scheme 1) of $[ZrCp''_2(CO)_2]$ (I); (ii) the formation of I by deoxygenation of CO_2 (method 4, Scheme 1) (cf. ref. 4 for related reactions); (iii) the first record of a ^{13}C NMR chemical shift (in I) for a Group IV transition metal carbonyl; (iv) the characterisation (Table 1) of I, $[ZrCp'_2(CO)_2]$

---

*No reprints available.



SCHEME 1. Routes and yields, under ambient conditions, to η-bis[bis(trimethylsilyl)cyclopentadienyl]dicarbonylzirconium(II) (I), and two typical reactions of complex I. Abbreviations: Cp″ = η-$C_5H_3(SiMe_3)_2$, COT = cyclooctatetraene, THF = tetrahydrofuran. Compound V has not yet been isolated as a pure compound, but as a mixture (ca. 1/1) with compound I; compound V has ν(CO) at 1842 cm^{-1} (n-C_6H_{14}) and $\delta(^{31}P)$ −143.8 ppm rel. to $P(OMe)_3$.

TABLE 1

CHARACTERISATION OF THE NEW METALLOCENE(II) CARBONYLS

Compound	M.p. (°C)	Colour	ν(CO) (cm^{-1})[a]	^{1}H NMR[c] (δ, ppm) $C_5H_{5-n}(SiMe_3)_n$	SiMe$_3$	^{13}C NMR[c] (δ, ppm) CO
$[ZrCp''_2(CO)_2]$ (I)	110—115 (dec.)	Dark green	1962, 1875[b]	5.60	0.10	264.4
$[ZrCp'_2(CO)_2]$ (II)	95—97 (dec.)	Dark brown	1970, 1880[b]	5.1 (m)[d]	0.16	
$[HfCp''_2(CO)_2]$[e]		Green	1950, 1855	5.35	0.10	

[a] Nujol. [b] In n-C_6H_{14}: for I 1965 and 1878 cm^{-1}, and for II 1972 and 1885 cm^{-1}. [c] C_6D_6 (shifts rel. to $SiMe_4$). [d] m = multiplet. [e] Not obtained free from $[HfCp''_2Cl_2]$ and $[ZrCp''_2(CO)_2]$, but composition of mixture readily determined from IR and ^{1}H NMR spectra.

(II), and $[HfCp''_2(CO)_2]$ (III) (obtained thus far only in a mixture); (v) the demonstration that $[HfCp''_2Cl_2]$ is reduced much less readily than $[ZrCp''_2Cl_2]$ (which may possibly provide a method for separating Zr from Hf and thus obtain the latter pure); commercial samples of $HfCl_4$ invariably contain appreciable $ZrCl_4$ contamination [5]; and (vi) two typical reactions of complex I (Scheme 1), which demonstrate its potential as a precursor to other zirconocene(II or IV) complexes, exemplified by $[ZrCp''_2I_2]$ (IV), and $[ZrCp''_2(CO)(PMe_3)]$ (V), (the latter has not yet been isolated as pure crystals).

The complexes $[MCp_2(CO)_2]$ have been obtained from $[MCp_2Cl_2]$ and either (i) Na—Hg and CO (1.5 atm) (in low yield, increased to 11%, at high pressure of CO [6]), or (ii) Li under high pressure of CO (200 atm, 80%) [7]. It is interesting, therefore, that progressive substitution in $\bar{C}_5H_5$ affords under ambient conditions $[ZrCp''_2(CO)_2]$ or $[ZrCp'_2(CO)_2]$ in high (Scheme 1) or moderate (50%) yield, respectively. However, $[ZrCp^\star_2(CO)_2]$ was likewise prepared in good yield from $[ZrCp^\star_2Cl_2]$ and Mg—$MgCl_2$ [2].

We are actively studying the chemistry of $[ZrCp''_2(CO)_2]$, as a substrate for Zr^{II}, Zr^{III}, and Zr^{IV} compounds. For the present, the potential of the carbonyl is illustrated by (i) an oxidative elimination ($(CO)_2/(I^-)_2$ exchange) and (ii) a neutral ligand displacement reaction (CO/PMe_3 exchange) (Scheme 1).

Acknowledgements. We thank the Spanish Government for a fellowship for A.A.; S.E.R.C. and I.C.I. (Plastics and Petrochemicals) PLC for a C.A.S.E. grant to D.J.W.W., and Drs. J. McMeeking and J. Segal for their interest.

References

1 Cf., D.J. Cardin, M.F. Lappert, P.I. Riley, and C.L. Raston, in G. Wilkinson, F.G.A. Stone, and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, 1982, Vol. 3, pp. 611—616.

2 D.J. Sikora, M.D. Rausch, R.D. Rogers, and J.L. Atwood, J. Amer. Chem. Soc., 103 (1981) 1265 and refs. therein.

3 M.F. Lappert, A. Singh, J.L. Atwood, and W.E. Hunter, J. Chem. Soc., Chem. Commun., (1981) 1190.

4 T. Ito and A. Yamamoto in S. Inoue and N. Yamazaki (Eds.), Organic and Bio-organic Chemistry of Carbon Dioxide. Wiley, New York, 1982, pp. 100—101; B. Demerseman, G. Bouquet, and M. Bigorgne, J. Organomet. Chem., 145 (1978) 41.

5 M.F. Lappert, P.I. Riley, and P.I.W. Yarrow, J. Chem. Soc., Chem. Commun., (1979) 305.

6 J.L. Thomas and K.T. Brown, J. Organomet. Chem., 111 (1976) 297.

7 B. Demerseman, G. Bouquet, and M. Bigorgne, J. Organomet. Chem., 107 (1976) C19.