Journal of Organometallic Chemistry, 184 (1980) C1—C2

Preliminary communication

THE PREPARATION OF A DI(CYCLOPENTADIENYL)ZIRCONIUM METHYLENE SPECIES FROM A PHOSPHORANE

JEFFREY SCHWARTZ* and KERRIE I. GELL
Department of Chemistry, Princeton University
Princeton, New Jersey 08544 (U.S.A.)

(Received August 30th, 1979)

SUMMARY

$Cp_2Zr(PPh_2Me)_2$ reacts with $CH_2{=}PPh_3$ to give $Cp_2Zr({=}CH_2)(PPh_2Me)$, the first example of a Group IV metal carbene complex.

Carbene complexes of transition metals from every group of the periodic table are known [1,2] with the notable exception of those from Group IV. We report herein the synthesis of the first example of such a species derived from a Group IV metal.

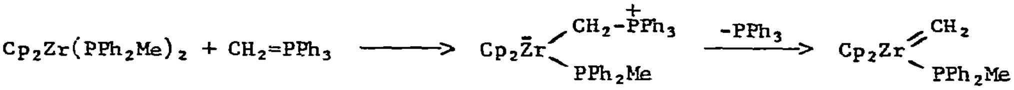
We recently described [3] the preparation of labile di(cyclopentadienyl)zirconium bis(phosphine) complexes, Cp_2ZrL_2, 1. These Zr(II) species are isoelectronic with, and presumably structurally analogous to, the known alkylidene complexes, $Cp_2Ta(CHR)R'$ [2]. Replacement of a phosphine ligand of Cp_2ZrL_2 by a "carbene" should, in theory, produce a Zr(II)(carbene) complex (an analogous reaction has been used [2] to prepare tantalum carbene complexes). Indeed, $Cp_2Zr({=}CH_2)(PPh_2Me)$, 2, is produced as a reactive, non-isolable compound (in approx. 40% yield, by NMR) on treatment of a benzene solution of $Cp_2Zr(PPh_2Me)_2$, 1, with an excess of the phosphorane, $Ph_3P{=}CH_2$, (15 equiv) at 42° C. The black solution of 2 slowly turns red-brown as 2 decomposes over a period of about 1 h.

Correlation of ^1H, ^{13}C and ^{31}P NMR data enabled identification of 2 and its spectral characterization in solution [^1H NMR (benzene-d_6) δ 11.0 (2, d, $Zr{=}C\underline{H}_2$, $^3J_{PH} = 4.8$ Hz), 5.50 (10, d, Cp, $^3J_{PH} = 1.6$ Hz), phosphine resonances obscured by excess phosphorane; ^{13}C NMR δ 248.6 (d, $Zr\text{-}\underline{C}H_2$, $^2J_{PC} = 14.6$ Hz; $^1J_{CH} = 121$ Hz, measured from ^1H NMR in reaction with $Ph_3P{=}^{13}CH_2$); ^{31}P NMR δ 34.2]. Irradiation of this P collapsed the ^1H resonance at δ 11.0 to a singlet, as well as collapsing the doublet for the Cp groups of the product. Other ^{31}P-^1H coupling in the spectrum (*e.g.*, in

$Cp_2Zr(PPh_2Me)_2$, PPh_2Me and $CH_2{=}PPh_3$) was unaffected. As well, irradiation of these other P nuclei had no effect on the ^1H doublets at δ 11.0 and δ 5.50. Therefore, there is only one P atom per molecule of the product 2; it is spectrally analogous to Group V carbene complexes [2].

During decomposition of 2 methane (≤ 10% based on Cp_2ZrL_2 and traces of ethylene and ethane are produced. Using $Ph_3P{=}^{13}CH_2$ as a reactant, major ^{13}C-enriched decomposition products having ^{13}C NMR signals consistent with the structural units Zr-CH_2-Zr (δ 173.1, $^1J_{CH}$ = 119.5 Hz)† and Zr-CH_3 (δ 16.6, $^1J_{CH}$ = 117 Hz) were identified [hydrolysis of the material formed on decomposition of 2 with tert-butanol produces methane (42% based on starting Cp_2ZrL_2), confirming the presence of metalated methane precursors].

The synthesis of 2 presumably proceeds via the ylid species 3, which loses triphenylphosphine. This suggests that the carbene ligand in 2 is of low electrophilicity,‡ as are those in Group V complexes [2]. Complex 2, in fact, behaves as a nucleophile: Solutions containing 2 react with methyl iodide, giving mixtures which produce substantial yields of ethane on hydrolysis.



1 3 2

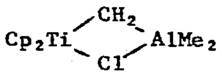
We are investigating the generality of this synthetic method for obtaining other carbene complexes of Group IV metals.

Acknowledgment. The authors gratefully acknowledge support for this work provided by the National Science Foundation (CHE 76-02130), and J. M. Pollock for data analysis.

REFERENCES

1. D. J. Cardin, B. Cetinkaya and M. F. Lappert, Chem. Rev., 72 (1972) 454.
2. P. R. Sharp and R. R. Schrock, J. Organometal. Chem., 171 (1979) 43.
3. K. I. Gell and J. Schwartz, J. Chem. Soc., Chem. Commun., (1979) 244.
4. F. N. Tebbe, G. W. Parshall and G. S. Reddy, J. Amer. Chem. Soc., 100 (1978) 3611.
5. N. J. Cooper and M. L. H. Green, J. Chem. Soc., Chem. Commun., (1974) 761.

---

† Spectral properties for the related complex  have been reported [4].

‡ Compare with the methylene ligand in a postulated [5] (tungstenocene)-(carbene) complex. This ligand is sufficiently electrophilic to be trapped by Me_2PhP to give a stable (tungstenocene)(ylid) species.