Tetra(tert-butyl)zirconium: Synthesis, Characterisation and Reaction with Carbon Dioxide

PETER BOUGEARD, JOHN J. McCULLOUGH, BRIAN G. SAYER and MICHAEL J. McGLINCHEY*

Department of Chemistry, McMaster University, Hamilton, Ont., L8S 4M1 Canada

Received February 21, 1984

The reaction of zirconium tetrachloride with t-butyllithium in diethyl ether at −78 °C gives the very unstable molecule (t-Bu)$_4$Zr. This product was characterised by ^{13}C and ^{91}Zr NMR spectroscopy and could be partially stabilised as its bis-pyridine adduct. Treatment of (t-Bu)$_4$Zr with carbon dioxide at −78 °C followed by acid hydrolysis gives predominantly the ketone, (t-Bu)$_2$CO. In contrast, other R$_4$Zr complexes (R = benzyl or allyl) under the same conditions yield equimolar amounts of the carbinol R$_3$COH and carboxylic acid RCO$_2$H almost quantitatively. The reaction of CO$_2$ with a mixture of R$_4$Zr complexes did not yield any cross-over products suggesting that an intramolecular mechanism is operative. A mechanistic scheme is proposed to account for all these observations.

Introduction

In recent years the factors controlling the stability of homoleptic transition metal alkyls have been established [1, 2]. Generally, alkyl groups possessing β-hydrogen atoms do not yield stable complexes since they decompose readily via transference of a β-hydrogen to the metal with subsequent elimination of an alkene. Normally these decomposition pathways can be blocked by use of alkyl groups such as $(CH_3)_3$-C–CH_2 or $(CH_3)_3Si$–CH_2. However, some systems have been reported in which, even though β-hydrogen atoms are present, the adoption of a molecular conformation compatible with alkene formation is sterically hindered. Thus, tetra(t-butyl)chromium is isolable [3]. In contrast, it has been noted [4] that for (t-butyl)$_3$Ln, where Ln = Er, Yb, Sm, it is necessary to incorporate tetrahydrofuran ligands to occupy the vacant sites and thus render the required geometry energetically inaccessible.

We now report the synthesis of tetra(t-butyl)-zirconium and its isolation and characterisation as the bis-pyridine adduct. Furthermore, we describe its reaction with carbon dioxide and note the difference between this reaction and the corresponding carboxylation reactions with tetrabenzyl- and tetra-allyl-zirconium. The mechanistic implications of these data are discussed.

Results and Discussion

Stable homoleptic t-butyl transition metal complexes are very rare. To our knowledge, the only documented examples are those reported by Kruse [3] and by Evans [4]. These results clarified the requirements for stable t-butyl complexes. If the central metal is small, as in (t-Bu)$_4$Cr, there will be an intermeshing of the methyl groups of the bulky t-butyl ligands hence making it difficult to achieve the transition state geometry required for β-hydrogen migration. In contrast, for large lanthanides Evans has shown that a coordinating solvent is necessary to occupy the vacant sites on the metal and thus vitiate the decomposition process.

The reaction of t-butyllithium with zirconium tetrachloride in diethyl ether at −78 °C yields a red solution which is extremely air-, light-, moisture- and thermally sensitive; indeed, the product decomposes in solution over a several hour time period even at −78 °C. However, ^{13}C and ^{91}Zr NMR spectra were obtained at −90 °C. The former technique showed the presence of a t-butyl compound different from t-BuLi [5] and we initially assigned the product as (t-Bu)$_n$ZrCl$_{4-n}$. The latter technique, *viz.*, ^{91}Zr NMR spectroscopy, has recently been developed in this laboratory [6]. The ^{91}Zr NMR spectrum of the red solution exhibited a single resonance at 799 ppm [7] with a half-width of ~45 Hz which, upon proton decoupling, decreased to ~20 Hz. The very narrow linewidths observed led us to assign the molecule as (t-Bu)$_4$Zr. Mislow [8] has calculated that in (t-Bu)$_4$M systems the alkyl groups would mesh so as to minimise steric interactions and give a molecule of T rather than T_d symmetry. This might account for the residual linewidth of ~20 Hz after proton decoupling since Zr(BH$_4$)$_4$, which is a regular tetrahedron, yields a ^{91}Zr resonance only 5 Hz wide when the ^{1}H and ^{11}B nuclei are decoupled [6b].

*Author to whom correspondence should be addressed.

0020-1693/84/$3.00

To confirm the assignment of the product as $(t\text{-}Bu)_4Zr$ it was isolated as its bis-pyridine adduct. It is well-documented [9] that tetra-alkyl zirconium compounds are stabilised by bipyridyl. The product of the reaction of $(t\text{-}Bu)_4Zr$ and excess pyridine is a single compound of moderate thermal stability whose ^1H NMR spectrum indicated the presence of pyridine and t-butyl moieties in the ratio 1:2; the ^{13}C and ^{91}Zr NMR data also indicated that only one product was formed.

The infrared spectrum of the bis(pyridine) complex is in accord with the reported data for the well-characterised tetra-alkylzirconium [10] or trialkyllanthanide complexes [4]. The mass spectrum did not yield a parent peak but the fragmentation pattern was entirely consistent with the formulation as $(t\text{-}Bu)_4Zr(py)_2$. The absence of a parent peak is not surprising in view of the fact that tetra-allylzirconium also fragments very readily in the course of electron impact mass spectrometry; the parent peak only becomes large under field-ionisation conditions. Neither the mass spectrum nor qualitative analysis gave any evidence for the presence of chlorine, and furthermore the yield of lithium chloride from the original low-temperature synthesis was determined gravimetrically and corresponded to the required 4:1 stoichiometry. We thus conclude that the reaction of $ZrCl_4$ with t-BuLi yields $(t\text{-}Bu)_4Zr$.

It was reported some time ago that tetrabenzylzirconium, *1*, reacts with carbon dioxide to yield, upon hydrolysis, equimolar quantities of phenylacetic acid and tribenzylcarbinol [12]. Since we were unaware of any other reports of the reaction of tetra-alkylzirconiums with carbon dioxide we decided to extend the investigations in this area.

We have repeated the above reaction and confirmed the results reported by Zucchini, Albizzati and Giannini [12]. Thus when carbon dioxide was bubbled through a cold (−78 °C) solution of *1* in ether, in the absence of light, the initially yellow solution gradually decolorised, over a 3–4 h period and a white precipitate was formed. Acid hydrolysis yielded almost stoichiometric quantities of phenylacetic acid and tribenzylcarbinol in approximately equal amounts. Similarly, treatment of tetra-allylzirconium, *2*, with carbon dioxide followed by acid hydrolysis gave excellent yields of 3-butenoic acid and tris-allylcarbinol in similar amounts:

$$R_4Zr \xrightarrow[2)\ HCl(aq)]{1)\ CO_2} RCO_2H + R_3COH + ZrOCl_2$$

1	R = $PhCH_2$	50%	50%
2	R = C_3H_5	55%	45%

In contrast, the reaction of tetra-t-butylzirconium with carbon dioxide, upon hydrolysis yielded the appropriate carboxylic acid (trimethyl acetic acid) together with di-t-butyl ketone (identified as its 2,4-dinitrophenylhydrazone derivative) and trace quantities of t-butanol. The lack of tris(t-butyl)carbinol is not entirely surprising in view of the very low yields obtained via other synthetic procedures, [13], and is presumably attributable to steric problems.

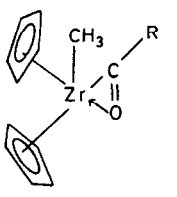
The formation of trialkylcarbinols in the reactions of main group homoleptic alkyls with carbon dioxide is a rare occurrence. Indeed, it is only with the aluminum trialkyls that trialkylcarbinol formation occurs in significant amounts and, even here, three mol of trialkylaluminum are required per mol of carbinol produced [14].

$$Et_3Al \xrightarrow{CO_2} Et_2Al{-}OCOEt \xrightarrow{2AlEt_3}$$

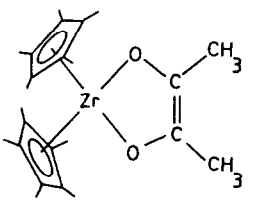
$$Et_2Al{-}O{-}AlEt_2 + Et_3CO{-}AlEt_2 \xrightarrow{H_2O} Et_3COH$$

Since it had already been established [12] that the stoichiometry of the present reaction involved one mol of tetrabenzylzirconium for every two mol of carbon dioxide, it is clear that the mechanistic pathways for the Al and Zr reactions are different.

In the latter case the initial reaction is almost certainly the attachment of a molecule of carbon dioxide to the coordinatively unsaturated zirconium centre; this must be rapidly followed by an intramolecular nucleophilic substitution to give the carbon dioxide insertion product, as shown in Scheme 1. The second migration must be mediated by the high oxophilicity of zirconium as reflected in the quoted value of ~550 kJ/mol for the strength of the Zr–O bond [15]. Further evidence supporting the second alkyl group migration is seen in the acyl complex, *3*, [16]; the carbonyl oxygen of this complex lies only 2.29 Å from the zirconium suggesting a reasonable degree of bonding between the two. Such a interaction would imply a certain electron deficiency at the carbonyl carbon and, indeed, this is reflected in the 180 cm^{-1} shift to lower frequency of the C–O stretch in *3* relative to that normally found for an acyl moiety. Bercaw has shown that coupling, as if between two carbenoid centres, can occur to give the complex *4* [17]. Further examples of the enhanced reactivity of carbonyl groups bound to zirconium have been reported by Erker and Rosenfeldt [18].



3



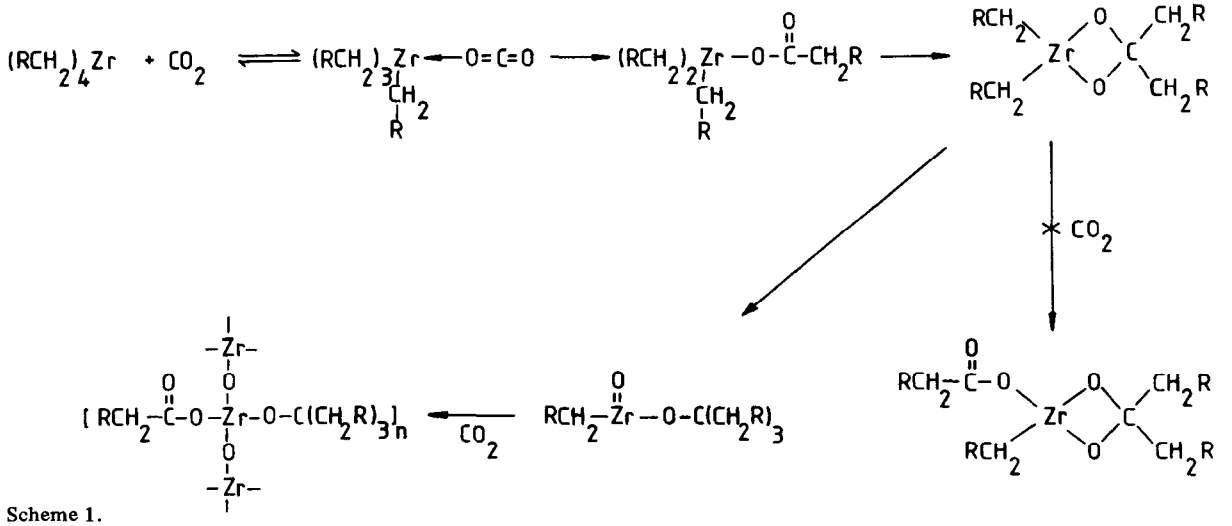
4

The thermodynamic driving force for the third migration is the formation of yet another Zr–O bond. In Scheme 1 we rather naively depict this as a Zr=O double bond whereas it is almost certainly an oxygen bridged telomer which can hydrolyse to give the observed products. Attempts to elucidate the structure of the proposed telomer, from the reaction of tetrabenzylzirconium with carbon dioxide using infra-red spectroscopy did not reveal definitive information. The only bands that could be identified with any certainty where those associated with a zirconium bound carboxylate (ν_{CO} 1595$_{asymmetric}$, 1450$_{symmetric}$ cm^{-1}) and a Zr–O–C stretch (ν_{Zr-O-C} 1020 cm^{-1}) assignable to a zirconium alkoxide [19, 20]. In the case of tetra(t-butyl)zirconium there is very little evidence of the third migration despite its strong driving force. This is attributed to the bulkiness of the t-butyl group which inhibits the final migration. The first two migrations occur quite readily since they relieve the steric crowding around the central zirconium atom but the third migration would result in an even more unfavourable situation since the central carbon atom is significantly smaller than the zirconium atom.

at comparable rates, were together treated with carbon dioxide. However, when tetra-t-butyl- and tetrabenzylzirconium were mixed together and treated with carbon dioxide the products were those observed in the earlier separate experiments. No mixed products, benzyl-t-butyl ketone or dibenzyl-t-butylcarbinol could be detected indicating that the reaction is primarily intramolecular. In particular, we note that although dibenzyl-t-butylcarbinol can be independently synthesised in respectable yield and gives a characteristic AB pattern for the methylene protons, attempts at the independent synthesis of benzyl-di-t-butylcarbinol were unsuccessful, presumably because of the extreme steric crowding.

$$R_4Zr + R'_4Zr \xrightarrow[2.HCl]{1.CO_2} R{-}C(=O){-}R' + R{-}C(OH)(R'){-}R + R'{-}C(OH)(R){-}R'$$

In contrast to the tetra-alkylzirconium complexes described above the rate of reaction of the tetra-allylzirconium complex is approximately an order of magnitude faster. The greatly enhanced reactivity



Scheme 1.

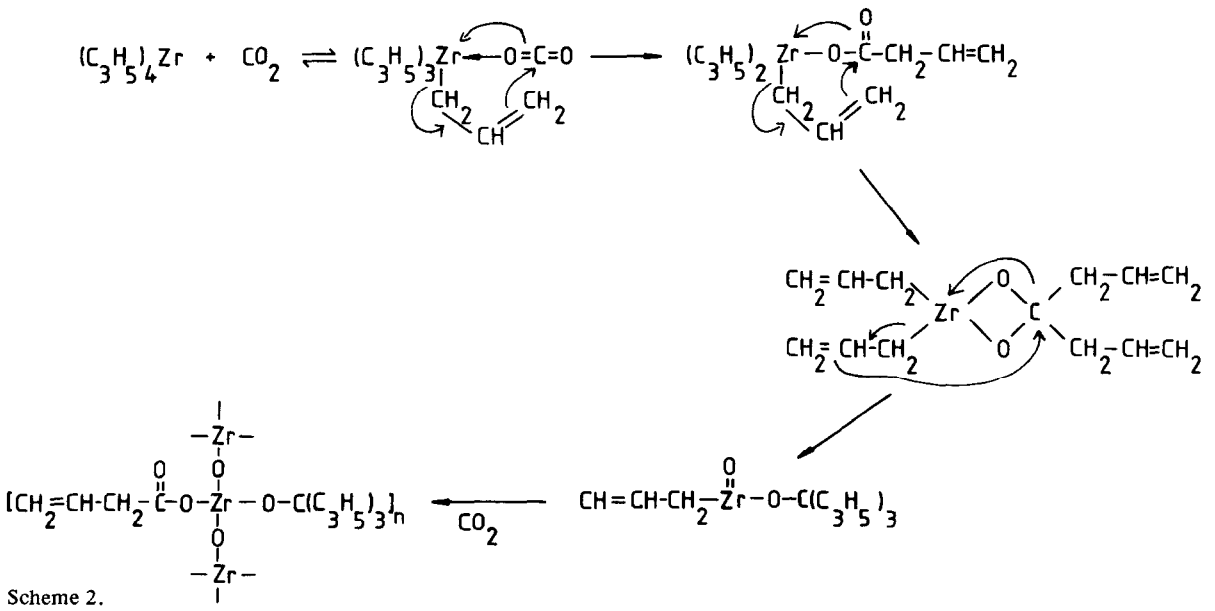
In the case of tetrabenzylzirconium, hydrolysis of the reaction mixture before completion yielded phenylacetic acid and tribenzylcarbinol as before, together with toluene (from hydrolysis of the $PhCH_2$–Zr bond) and benzyl alcohol (arising from reaction of the alkylzirconium with traces of oxygen). No dibenzyl ketone was observed indicating that the formation of the carbinol is very rapid.

Whilst the above observations indicate an intramolecular process, there is still a possibility of an intermolecular component at some stage in the reaction. In order to answer this question a cross-over experiment was performed in which two different tetra-alkyl zirconium complexes, which reacted

of the tetra-allylzirconium has been noted previously by Ballard [21] who attributed it to the ambidentate character of the σ-allyl group. Indeed, the reaction of tetra-allylzirconium with esters to give carbinols provides ample precedent for the mechanism proposed here. The alternative pathway available for the tetra-allylzirconium (Scheme 2) can in fact be viewed as being analogous to a Claisen rearrangement.

Experimental

The synthesis and manipulation of all tetra-alkylzirconium complexes were carried out in an atmo-



Scheme 2.

sphere of prepurified nitrogen with rigorous exclusion of air, moisture and light. All solvents were thoroughly dried in a manner appropriate to each [22]. ^{1}H NMR spectra were recorded on a Varian EM390 spectrometer; ^{13}C and ^{91}Zr NMR spectra were obtained using Bruker WP80 and WM250 spectrometers operating at 20.115 and 23.325 MHz, respectively. Infrared spectra were measured on a Perkin-Elmer 337 spectrometer. Melting points are uncorrected. Mass spectrometry was performed on a VG Micromass 7070 spectrometer equipped with a VG 2035 data system; the electron energy was 70 eV and the ion source temperature was 200 °C.

Preparation of Tetra-allylzirconium

Tetra-allylzirconium was prepared as described by Becconsall *et al.* [11].

Preparation of Tetrabenzylzirconium

Tetrabenzylzirconium was prepared as described by Zucchini *et al.* [12].

Preparation of Tetra(t-butyl)zirconium

To a suspension of zirconium tetrachloride (1.5 g, 0.0065 mol) in diethyl ether (25 cm^3) at −78 °C was added, dropwise, a pentane solution of t-butyllithium (0.030 mol). After stirring for 1.5 h the reaction mixture was filtered at low temperature to give a reddish yellow solution of tetra(t-butyl)-zirconium.

^{13}C NMR: Et_2O, 183 K; δ 24.5 (CH_3); 96.0 (C–Zr); ^{91}Zr NMR {^{1}H}: Et_2O, 183 K; +799 ppm relative to Cp_2ZrBr_2, $W_{1/2} \sim 20$ Hz.

Tetra(t-butyl)zirconium was filtered at −78 °C, treated with pyridine (2.0 g, 0.25 mol) and allowed to warm slowly to room temperature. The ether was removed *in vacuo* to yield a dark red solid (2 g; 65%) of moderate thermal stability. ^{1}H NMR: C_6D_6, δ 1.45 (36H, t-Bu) and complexed pyridine resonances at δ 6.75 (4H, β-H), 7.1 (2H, γ-H), 8.6 (4H, α-H); ^{13}C NMR: C_6D_6, δ 149.7 (α-C_5H_5N), 136.5 (γ-C_5H_5N), 121.3 (β-C_5H_5N), 119.4 (C–Zr), 31.0 (CH_3); ^{91}Zr NMR: C_6D_6, +617, $W_{1/2} \sim 3900$ Hz; major mass spectral peaks at: *m/e* (%), 283(1) $C_{13}H_{23}NZr^+$; 261(2) $C_{12}H_{27}Zr^+$; 248(1) $C_{10}H_{10}N_2Zr^+$; 226(3) $C_9H_{14}NZr^+$; 169(25) $C_5H_5NZr^+$; 147(18) $C_4H_9Zr^+$; 90(10) Zr^+; 79(49) $C_5H_5N^+$; 57(100) $C_4H_9^+$. All Zr containing fragments had the correct isotopic abundance patterns. IR cm^{-1}, C_6H_6, 3140(w), 2790(sh) 2740(s), 2790(m), 2690(w), 2660(m), 2600(m), 1640(m), 1575(m), 1425(m), 1360(m), 1275(s), 1210(w), 1090(m), 1065(w), 1038(w), 965(m), 900(m), 850(w), 780(w), 760(vw), 735(w), 570–520 (broad, three bands), 600–250 (broad, poorly resolved).

Reaction of Tetra-alkylzirconium with Carbon Dioxide

Carbon dioxide, obtained by evaporation of solid carbon dioxide, was bubbled through a freshly prepared solution of the tetra-alkylzirconium until the solution became colourless and a white precipitate had formed. The reaction mixture was then hydrolysed with 10% aqueous hydrochloric acid (v/v) and the diethyl ether layer separated. To ensure complete extraction of the organic products the aqueous layer was saturated with sodium chloride and extracted again using diethyl ether (3 × 25 cm^3). The combined extracts were dried ($MgSO_4$) and the ether removed by distillation.

The organic products were identified by NMR and IR spectroscopy. In the case of the $(t\text{-Bu})_4Zr$ reac-

tion, di-t-butyl ketone was characterized as its 2,4-dinitrophenylhydrazone (m.p. 130 °C). Furthermore, tris(allyl)carbinol was independently synthesized since the original literature preparation [23] did not provide spectroscopic data.

Cross-over Reaction Between Tetrabenzylzirconium and Tetra(t-butyl)zirconium

Freshly prepared solutions of tetrabenzylzirconium (0.004 mol) and tetra(t-butyl)zirconium (0.006 mol) were combined and the reaction carried out as described above.

Examination of the organic products by ^{1}H n.m.r. spectroscopy indicated that no cross-over products were present. For comparison purposes, possible cross-over products which had not previously been reported were synthesized as described below.

Preparation of Tris-Allylcarbinol

To a solution of ethyl chloroformate (5 g, 0.047 mol) in diethyl ether (100 cm^3) at 0 °C under nitrogen was added, dropwise over a period of 1 h, a diethyl ether solution of allyl magnesium bromide (0.141 mol). The reactants were stirred for a further 5 h and then decomposed using 20% hydrochloric acid (v/v). The layers were separated and the diethyl ether layer dried ($MgSO_4$). After removal of the diethyl ether, distillation of the residue yielded 4.2 g (20%) tris-allylcarbinol b.p. 78–82 °C/15 mm Hg; (lit. [8] 191–2 °C). ^{1}H NMR ($CDCl_3$) δ 5.7 (H_2, m), 5.0 (H_3, ddt), 4.9 ($H_{3'}$, dd), 2.1 (H_1, m), $^3J_{3,2}$ = 17.5 Hz, $^3J_{3',2}$ = 9.0 Hz, $^3J_{2,1}$ = 7.3 Hz, $^2J_{3,3'}$ = 3.0 Hz, $^4J_{3,1}$ = 1.9 Hz; mass spectrum, *m/z* (%) 135(25), 111(24), 93(20), 69(100).

Preparation of Benzyl-t-butyl Ketone

To a solution of trimethylacetylchloride (4.25 g, 0.036 mol) in diethyl ether (75 cm^3) under nitrogen was added anhydrous ferric chloride (0.03 g), and the reactants were heated to reflux. During 2 h, benzylmagnesium bromide (0.036 mol) in diethyl ether (100 cm^3) was added. The reactants were stirred at reflux for an additional 2 h and then decomposed by the addition of water. The layers were separated and the diethyl ether dried ($MgSO_4$). Distillation yielded 1.6 g (26%) benzyl-t-butyl ketone, b.p. 144–146 °C/15 mm Hg. ^{1}H NMR ($CDCl_3$) δ 7.2–7.0 (5H,b), 3.75(2H,s), 1.15(9H,s); ^{13}C NMR, δ 212.8 (CO), 135.1, 129.7, 128.5, 126.7 (phenyl), 44.7 (C–Me_3), 43.6(CH_2), 26.5 (CH_3's); Mass spectrum, *m/z* (%) 176(4), 91(40), 57(100); i.r., ν_{CO} 1715 cm^{-1}.

Preparation of Dibenzyl-t-butylcarbinol

To a solution of dibenzyl ketone (5 g, 0.024 mol) in diethyl ether (50 cm^3) at 0 °C under nitrogen was added, dropwise over a period of 1 h, a pentane solution of t-butyl lithium (0.024 mol). The reaction mixture was allowed to warm to room temperature, stirred for an additional 2 h and then decomposed by the addition of water. The layers were separated and the diethyl ether layer dried ($MgSO_4$). Complete purification of the alcohol was not achieved but characterisation by spectroscopic methods was possible; ^{1}H NMR ($CDCl_3$) δ 7.4–7.0 (10 H,m), 3.0, (H_A,d), 2.8 (H_B,d), J_{AB} = 13.5 Hz, 1.1 (9H,s); ^{13}C NMR, δ 138.6, 131.2, 128.3, 126.3 (phenyl), 77.9 (C–OH), 49.3 (C–Me_3), 41.8 (CH_2), 26.2 (CH_3); Mass spectrum, *m/z* (%) 250(2), 91(100), 57(45).

Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada for financial support through their Operating and Strategic Energy Grant programmes.

References

1 P. J. Davidson, M. F. Lappert and R. Pearce, *Acct. Chem. Res., 7,* 209 (1974).
2 P. J. Davidson, M. F. Lappert and R. Pearce, *Chem. Rev., 76,* 219 (1976).
3 W. Kruse, *J. Organomet. Chem., 42,* C39 (1972).
4 W. J. Evans and A. L. Wayda, *J. Am. Chem. Soc., 100,* 7121 (1978).
5 S. Bywater, P. Lachance and D. J. Worsfold, *J. Phys. Chem., 79,* 2148 (1975).
6 a) B. G. Sayer, Hao Nguyen, G. Dénès, D. G. Bickley and M. J. McGlinchey, *Inorg. Chim. Acta, 48,* 53 (1981). b) B. G. Sayer, J. I. A. Thompson, Hao Nguyen, T. Birchall, D. R. Eaton and M. J. McGlinchey, *Inorg. Chem., 20,* 3748 (1981).
7 Relative to Cp_2ZrBr_2. The absolute frequency for this compound is 9.297300 MHz.
8 K. Mislow and L. D. Iroff, *J. Am. Chem. Soc., 100,* 2121 (1978).
9 J. F. Clarke, G. W. A. Fowles and D. A. Rice, *J. Organomet. Chem., 74,* 417 (1974).
10 M. R. Collier, M. F. Lappert and R. Pearce, *J. Chem. Soc. Dalton Trans.,* 445 (1973).
11 J. K. Becconsall, B. E. Job and S. O'Brien, *J. Chem. Soc. (A),* 423 (1967).
12 U. Zucchini, E. Albizzati and U. Giannini, *J. Organomet. Chem., 26,* 357 (1971).
13 P. D. Bartlett and A. Schneider, *J. Am. Chem. Soc., 67,* 141 (1945).
14 K. Ziegler, F. Krupp, K. Weyer and W. Larbig, *Justus Liebig's Ann. Chem., 629,* 251 (1960).
15 M. F. Lappert, D. S. Patil and J. B. Pedley, *J. Chem. Soc. Chem. Comm.,* 830 (1975).
16 G. Fachinetti, G. Fochi and C. Floriani, *J. Chem. Soc. Dalton Trans.,* 1946 (1977).
17 J. M. Manriquez, D. R. McAlister, R. D. Sonner and J. E. Bercaw, *J. Am. Chem. Soc., 100,* 2716 (1978).
18 G. Erker and F. Rosenfeldt, *J. Organomet. Chem., 224,* 29 (1982).

19 K. R. Naher, A. K. Solanki and A. M. Shandari, *Synth. React. Inorg. Met.-Org. Chem.*, *12*, 805 (1982).
20 C. G. Barraclough, D. C. Bradley, J. Lewis and I. N. Thomas, *J. Chem. Soc.*, 2601 (1961).
21 D. G. H. Ballard, W. H. Janes and T. Medinger, *J. Chem. Soc. (B)*, 1168 (1968).
22 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, 'Purification of Laboratory Chemicals', 2nd Edition, Pergamon Press, Oxford, 1980.