Reaction of Monoborane with Tris(cyclopentadienyl)uranium(IV) Derivatives

Marina Porchia,* Nicola Brianese, Franco Ossola, Gilberto Rossetto, and Pierino Zanella
Istituto di Chimica e Tecnologia dei Radioelementi del C.N.R., Corso Stati Uniti—35100 Padova, Italy

The compounds [$UX(cp)_3$] (cp = η^5-cyclopentadienyl; X = Me, Et, Ph, NEt_2, OMe, F, $CONEt_2$, or COBu) react in toluene at room temperature with the labile adducts BH_3•L (L = tetrahydrofuran, BH_3, or Me_2S) giving the well known product [$U(BH_4)(cp)_3$], whereas [$UX(cp)_3$] (X = Cl, Br, or I) seem to be unreactive even at high temperature. In some cases (X = Me, Et, or Ph), intermediate species such as [$U(BH_3X)(cp)_3$] were detected. A general reaction mechanism involving a hydride-bridged intermediate is proposed.

The reactivity of BH_3•L (L = Lewis base) towards organometallic and co-ordination compounds shows various aspects. The M–H, M–C, and M–O bond of hydride,[1] hydrocarbyl,[2] and alkoxide[3] derivatives may be directly involved in the formation of tetrahydroborate. In some cases such derivatives may react further giving more complex metal hydroborates MB_3H_8;[4] in addition, reduction[3] of the metal ion may occur. On the other hand, interactions with co-ordinated ligands without apparent participation of the central metal, in which, *e.g.*, acyl ligands undergo hydrogenation to alkyl ligands,[5] have recently been described. We have previously published preliminary results on the reaction of borane with [$UX(cp)_3$][6] (X = Me or Et, cp = η^5-cyclopentadienyl) which generally reflects the features of the corresponding reaction with [$ZrMe_2(cp)_2$]. As in both cases a hydride-bridged intermediate is proposed, we have extended our study to a series of [$UX(cp)_3$] compounds in order to obtain further information about the influence of the electronic nature of the U–X bond, and in some cases of the hapticity of the ligand X, on the reaction path. Parallel experiments were carried out by using the Lewis acids $B(OR)_3$ (R = Me or Bu).

Experimental

All the operations were carried out in nitrogen-filled glove-boxes with the rigorous exclusion of oxygen and moisture. Solvents and common materials were appropriately dried, purified, and handled as previously described.[7] The [$UX(cp)_3$] derivatives were synthesized according to published procedures;[7a,b] the iodide was prepared from [$U(AlH_4)(cp)_3$][7c] and MeI suspended in Et_2O. Borane–dimethyl sulphide in toluene solution was titrated with t-butylamine and used without further purification, as was borane–tetrahydrofuran (thf) (Janssen products). We preferred BH_3•Me_2S because of its high stability with respect to the other BH_3 complexes. Commercially available tributyl and trimethyl borate (Janssen) were used as supplied. Solvent-free diborane was obtained by *in situ* thermal decomposition of $SnR_2(BH_4)_2$.[8]

Proton and ^{11}B n.m.r. spectra were recorded on a Varian FT 80A spectrophotometer; ^1H chemical shifts are referred to C_6D_5H as internal standard, ^{11}B chemical shifts to BF_3•Et_2O as external standard (in the latter case a positive sign corresponds to a low-field shift). Sample solutions, prepared inside the glove-boxes were manipulated in tubes capped or sealed under vacuum. Infrared spectra were recorded on a Perkin-Elmer 580 B spectrometer using Nujol mulls sandwiched between KBr plates in an air-tight O-ring holder. The reaction products were identified by ^1H and ^{11}B n.m.r. spectroscopy. Unfortunately, experimental problems prevented a satisfactory identification of non-uranium products. However, we believe that, although very useful, this is not essential to the aim of the present work.

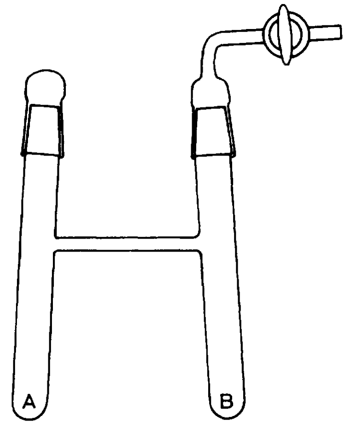


Figure. H-Shaped vessel for reactions with solvent-free B_2H_6

As the same conditions were adopted for all the reactions, the results of which are collected in the tables, standard procedures are described only for typical experiments. All reactions were carried out at room temperature unless specified otherwise.

[$U(NEt_2)(cp)_3$] + BH_3•Me_2S.—The compound [$U(NEt_2)(cp)_3$] (505 mg, 1 mmol) was dissolved in toluene (10 cm^3) together with BH_3•Me_2S (1 mmol). The mixture was stirred for several hours and from time to time, aliquots were removed and the solvent was evaporated under vacuum; the residue was redissolved into C_6D_6 and the ^1H (and sometimes ^{11}B) n.m.r. spectrum was recorded. Progressive consumption of [$U(NEt_2)(cp)_3$] led to concomitant formation of [$U(BH_4)(cp)_3$].

[$UPh(cp)_3$] + BH_3•Me_2S.—The compound [$UPh(cp)_3$] (510 mg, 1 mmol) was dissolved in toluene (10 cm^3) together with BH_3•Me_2S (1 mmol). Monitoring the sample as above revealed the disappearance of [$UPh(cp)_3$] and the contemporary formation of [$U(BH_4)(cp)_3$] and of [$U(BH_3Ph)(cp)_3$] identified on the basis of its reported ^1H n.m.r. and i.r. spectra.[9] The ^{11}B n.m.r. spectrum showed a sharp quartet at +92.5 p.p.m.

[$UMe(cp)_3$] + *Solvent-free* B_2H_6.—The compound [$UMe(cp)_3$] (450 mg) was dissolved in toluene (10 cm^3) and placed in the nitrogen-cooled arm A of the H-shaped vessel shown in the Figure. In arm B, $SnBu_2Cl_2$ and $NaBH_4$ were mixed. The system was closed with a vacuum stopcock and evacuated. Heating of arm A to 160 °C initiated the reaction[8] between $SnBu_2Cl_2$ and $NaBH_4$, producing B_2H_6 which condensed into the cooled arm B. After stirring for some hours the solution was analysed by n.m.r. spectroscopy as above in order to determine the residue of [$UMe(cp)_3$]. Arm B was then recharged with

Table 1. Reactions between $[UX(cp)_3]$ and $BH_3{\cdot}Me_2S$[a]

X	Molar ratio $[UX(cp)_3]:BH_3{\cdot}Me_2S$	Reaction time (h)	Yield (%)		
			$[UX(cp)_3]$	$[U(BH_3X)(cp)_3]$	$[U(BH_4)(cp)_3]$
Ph	1:1	2	—	30	70
	1:1	24	—	20	80
	1:10	2	—	20	80
	1:10	24	—	—	100
OMe	1:1	24	18	—	82
	1:2	24	—	—	100
Cl, Br, or I	1:10[b]	48	100	—	—
F	1:2	2	—	—	100
COBu	1:1	24	22	—	78
	1:2	24	10	—	90
$CONEt_2$	1:1	24	52	—	48
	1:10	24	—	—	100
NEt_2	1:1	20	67	—	3
	1:1	120	60	—	40
	1:2	120	—	—	100
	1:4	40	—	—	100

[a] Conditions: solvent, toluene; room temperature, where not specified otherwise. The composition of reaction mixtures after incomplete product formation was deduced from the integrals of the cyclopentadienyl ^1H n.m.r. signals. For ^1H n.m.r. data for different $[UX(cp)_3]$ species see R. D. Fischer, in 'Fundamental and Technological Aspects of Organo-f-element Chemistry,' eds. T. J. Marks and I. L. Fragalà, NATO ASI series, D. Riedel, Dordrecht, 1984, vol. 155, p. 277 and refs. therein. [b] Upon reflux.

$SnBu_2Cl_2$ and $NaBH_4$ and the operation repeated until the $[UMe(cp)_3]$ had been totally consumed.

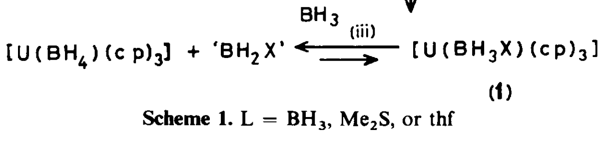
$[UMe(cp)_3] + BH_3{\cdot}Me_2S + B(OBu)_3$.—The adduct $BH_3{\cdot}Me_2S$ (1 mmol) and $B(OBu)_3$ (1 mmol) were mixed in toluene (10 cm^3) and stirred for 3 d at room temperature. The ^{11}B n.m.r. spectrum of the solution showed signals whose positions and shapes corresponded to the three species resulting from the equilibrium $BH_3 + 2B(OBu)_3 \rightleftharpoons 3BH(OBu)_2$.[10] At this point the solution was added to a toluene solution (10 cm^3) containing $[UMe(cp)_3]$ (0.045 g, 0.1 mmol). The mixture was stirred and analysed as described above; progressive consumption of $[UMe(cp)_3]$ gave $[U(OBu)(cp)_3]$ and $[U(BH_4)(cp)_3]$ (minor amount) as the only reaction products.

The use of $BH_3{\cdot}thf$, instead of $BH_3{\cdot}Me_2S$ or B_2H_6, led essentially to the same results. The only difference was that during the reaction between many $[UX(cp)_3]$ and commercial $BH_3{\cdot}thf$ (Janssen Chimica) the ^1H n.m.r. spectrum of $[U(OBu)(cp)_3]$ was observed, probably due to a side reaction of $[UX(cp)_3]$ with decomposition and hydrolysis products of $BH_3{\cdot}thf$ such as n-butyl borate. Independent reaction of various $[UX(cp)_3]$ with B_2H_6 in toluene–thf solution did not give rise to this species. The formation of $[U(OBu)(cp)_3]$ prevented a calculation of the exact ratio between different products in the reaction mixture and so the data concerning $BH_3{\cdot}thf$ are not reported in Table 1.

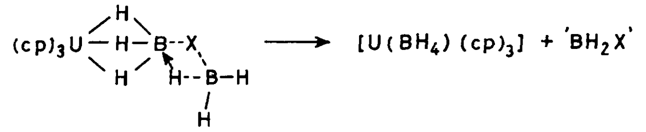
Results and Discussion

The results obtained together with the conditions for the reaction of $[UX(cp)_3]$ compounds with the borane derivatives are reported on Table 1. They indicate that: (*a*) for X = F, OMe, NEt_2, COBu, or $CONEt_2$ and L = Me_2S the reaction affords almost quantitatively $[U(BH_4)(cp)_3]$ as the final product under rather mild conditions, *i.e.* room temperature and a moderate excess of $BH_3{\cdot}L$ (analogous behaviour has been observed with $BH_3{\cdot}L$, L = BH_3 or thf); (*b*) for the halide series $[UX(cp)_3]$ (X = F, Cl, Br, or I) no reaction takes place, except for X = F, even under reflux and after a long time; (*c*) intermediate species of the type $[U(BH_3X)(cp)_3]$ have been unequivocally detected by ^1H and ^{11}B n.m.r. spectroscopy for X = Me,[6] Et,[6] or Ph.

Thus also for $[UPh(cp)_3]$ a reaction sequence analogous to that suggested for the reaction of $[UX(cp)_3]$ (X = Me or Et)[6] may be proposed. This behaviour is remarkable especially when compared with that of $[ZrPh_2(cp)_2]$ which is inert towards $BH_3{\cdot}thf$.[2a] The $[UX(cp)_3]$ (X = F, NEt_2, OMe, COBu, or $CONEt_2$) compounds give $[U(BH_4)(cp)_3]$ directly, without detection of any intermediates. Nevertheless a reaction mechanism analogous to that previously illustrated cannot be ruled out and can be adapted also for these $[UX(cp)_3]$ species (Scheme 1). The only difference is the intermediate (**1**) which has never been detected by ^1H and ^{11}B n.m.r. spectroscopy. This is probably due to its rapid consumption by the second BH_3 molecule with subsequent formation of $[U(BH_4)(cp)_3]$ [step



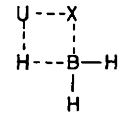
Scheme 1. L = BH_3, Me_2S, or thf



(B)

Scheme 2.

(iii)]. In particular, step (iii) could involve the transition state (**B**) (Scheme 2). The nature of the X group plays a fundamental role in the rate of step (iii) and above all the ability of X to form a partial bond with the boron atom of the incoming BH_3 is very important. Comparing carbon (in the case of X = alkyl or aryl) and a N, O, or F atom (X = NEt_2, OMe, F, $CONEt_2$, or COBu), only for the last atom is there the possibility of further co-ordination with boron because of the presence of unshared electron pairs; carbon can co-ordinate with a boron atom only through an electron-deficient bond. For this reason it can easily be argued that step (iii) is fast and so the intermediate (**1**), in contrast to $[U(BH_3Ph)(cp)_3]$, would have too short a life-time to be detected. The importance of the co-ordinating ability of the X group towards boron is evident also if we consider the series of halogen derivatives $[UX(cp)_3]$ (X = F, Cl, Br, or I), of which only the fluoride reacts with BH_3. Here the tendency to form bridged species* such as (**2**) seems to be reflected in the average bond energies: $D_{B\text{-}F} > D_{U\text{-}F}$ but $D_{B\text{-}X} < D_{U\text{-}X}$ (where X = Cl, Br, or I).[11]



(2)

As far as the reactions of acyl and carbamoyl derivatives are concerned, the behaviour of $[U(COR')(cp)_3]$ (R' = Bu or NEt_2) compounds is different from that of $[Zr(COMe)Me(cp)_2]$ which does not react directly with $BH_3{\cdot}L$, only after previous decarbonylation.[2a] We observed: (*a*) $[U(CONEt_2)(cp)_3]$ is stable towards decarbonylation, yet it forms $[U(BH_4)(cp)_3]$; (*b*) although $[U(COBu)(cp)_3]$ is in equilibrium with its decarbonylated form $[UBu(cp)_3]$,[7b] no $[U(BH_3Bu)(cp)_3]$ intermediate has been detected during the reaction. Thus we suggest a reaction pathway following Scheme 1 where (**1**) represents the species $[U\{BH_3(COBu)\}(cp)_3]$ and $[U\{BH_3(CONEt_2)\}(cp)_3]$ which undergo further reaction with BH_3 [step (iii)] to give $[U(BH_4)(cp)_3]$. In our opinion the fact that we did not find the intermediate $[U(BH_3Bu)(cp)_3]$ in a mixture containing both $[UBu(cp)_3]$ and $[U(COBu)(cp)_3]$ indicates that the latter reacts with $BH_3{\cdot}L$ faster than does $[UBu(cp)_3]$ supporting our previous hypothesis and demonstrating also that the presence of a bihapto ligand such as COBu or $CONEt_2$ instead of a monohapto ligand (such as Me, Ph, NEt_2, F, *etc.*) does not prevent BH_3 attack or modify the reaction path.

From the reaction scheme, theoretically 2 mol of BH_3 appear to be necessary to convert 1 mol of $[UX(cp)_3]$ into $[U(BH_4)(cp)_3]$. In most cases, about 70% conversion was observed by reaction with 1 mol of BH_3. Consequently the simple 1:2 stoicheiometry (1) should be replaced by the more

$$[UX(cp)_3] + 2BH_3 \longrightarrow [U(BH_4)(cp)_3] + BH_2X \quad (1)$$

appropriate (2) ($n = m + 1, m \leqslant 3$) which takes into account

$$m[UX(cp)_3] + nBH_3 \longrightarrow m[U(BH_4)(cp)_3] + (n - m)BH_{3-m}X_m \quad (2)$$

the possibility that borane species such as BH_2X or BHX_2 could replace BH_3 in step (iii) of Scheme 1. Such species, not detected unequivocally, might originate from complicated disproportionation equilibria[10,12] between BH_3 and BX_3 of the type (3)—(5). As far as the exact nature of the $BH_{3-m}X_m$

$$BX_3 + BH_3 \rightleftharpoons BX_2H + BH_2X \quad (3)$$

$$2BX_2H \rightleftharpoons BX_3 + BH_2X \quad (4)$$

$$2BXH_2 \rightleftharpoons BX_2H + BH_3 \quad (5)$$

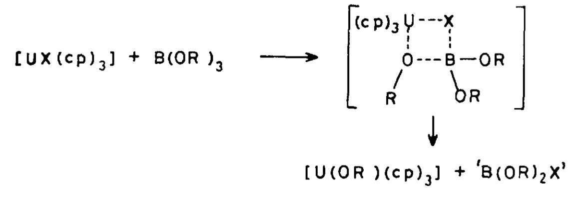
species is concerned we did not identify the uranium-free organic boron products. For X = COBu or $CONEt_2$ such species could be formulated as $BH_2(COBu)$ or $BH_2(CONEt_2)$, formally analogous to the acylboranes postulated as intermediates in a particular CO activation reaction.[13]

Table 2. Reactions between $[UX(cp)_3]$ and $B(OR)_3$[a]

X	R	Result
Me	Bu	*b*
Cl	Bu	*b*
BH_4	Bu	*b*
BH_3Me	Bu	*b*
OMe	Bu	$[U(OBu)(cp)_3]$[c]
NEt_2	Bu	$[U(OBu)(cp)_3]$[c]
COBu	Me	$[U(OMe)(cp)_3]$[c]
Me	*d*	$[U(BH_4)(cp)_3]$ + $[U(OBu)(cp)_3]$[c]
NEt_2	*d*	$[U(BH_4)(cp)_3]$ + $[U(OBu)(cp)_3]$[c]

[a] Conditions: solvent, toluene; room temperature; $B(OR)_3$ always in excess; reaction time > 24 h. Different $[UX(cp)_3]$ species identified as in Table 1. [b] No reaction. [c] Plus unidentified organoboron products. [d] BH_3–$B(OBu)_3$ mixture.

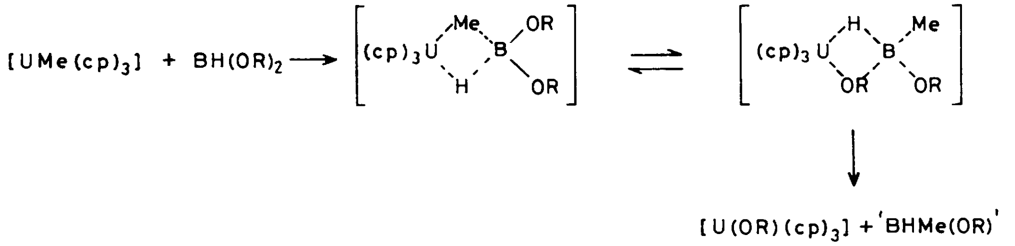
The proposed mechanism involving hydride- and boron-bridged species as intermediates is supported by the qualitative results (Table 2) obtained by replacing BH_3 by $B(OR)_3$ in the above reactions. It is noteworthy that: (*a*) when X = Me, Cl, BH_4, or BH_3Me no reaction occurs; (*b*) when X = OMe, NEt_2, or COBu reaction takes place with X/OR exchange; (*c*) the BH_3–$B(OR)_3$ mixture leads to formation of $[U(BH_4)(cp)_3]$ along with $[U(OR)(cp)_3]$ even when X = Me. So it appears that $B(OR)_3$ reacts with $[UX(cp)_3]$ only when X has marked bridging ability (O or N) toward boron, but not with alkyl or Cl, suggesting the reaction sequence in Scheme 3. The reason may be a reduced Lewis acidity of alkyl borates with respect to the borane. Regarding the reaction between $[UMe(cp)_3]$ and the BH_3–$B(OR)_3$ mixture, the formation of $[U(OR)(cp)_3]$ as the main product is surprising as $B(OR)_3$ is inert towards $[UMe(cp)_3]$, $[U(BH_3Me)(cp)_3]$ (an intermediate in the reaction with BH_3), and $[U(BH_4)(cp)_3]$. Thus we are inclined to



Scheme 3. X = OMe, NEt_2, or COBu

---

* The compound $[UF(cp)_3]$ shows a peculiar behaviour also in its ability to form dimeric fluorine-bridged species in solution (R. D. Fischer, R. V. Ammon, and B. Kanellakopulos, *J. Organomet. Chem.*, 1970, **25**, 123).



Scheme 4.

suggest the participation of $BH(OR)_2$, formed by the redistribution equilibrium (6)[10,12] which can lead to $[U(OR)(cp)_3]$

$$BH_3 + 2B(OR)_3 \rightleftharpoons 3BH(OR)_2 \qquad (6)$$

in Scheme 4. The ability of $BH(OR)_2$ to form H-bridged species seems to be indispensable for this reaction.

In conclusion we have shown that not only U–C_{alkyl} but also U–C_{phenyl}, U–OMe, U–NEt_2, U–COBu, U–$CONEt_2$, and U–F bonds are changed to U–BH_4 bonds by reaction with BH_3·L. Thus the investigated uranium derivatives generally behave similarly to the corresponding $[ZrMe_2(cp)_2]$[2a] derivatives. Moreover $[UPh(cp)_3]$ reacts with BH_3·L {like $[UMe(cp)_3]$ and $[UEt(cp)_3]$}, whereas $[ZrPh_2(cp)_2]$ is inert. This difference may be due to an enhanced co-ordinating ability of uranium with respect to zirconium, towards the hydride of BH_3, which makes up for the weaker ability of the phenyl group to form the intermediate $M(\mu\text{-}H)(\mu\text{-}Ph)BH_2$. A clear indication of the formation of the corresponding intermediate for M = U is the existence of the stable compound $[U(BH_3Ph)(cp)_3]$. Whereas Zr–COMe does not react with BH_3·L, we have evidence that U–COR′ (R′ = Bu or NEt_2) do react directly, even faster than U–R. Such strong bonds as U–O and U–N (hard Lewis acid–hard Lewis base) may be converted into U–H bonds of U–BH_4 (*i.e.* hard Lewis acid–soft Lewis base[14]).

The failure of $[Zr(COMe)Me(cp)_2]$ to react has been ascribed to the absence of empty *d* orbitals on Zr necessary for the initial co-ordination of the bridging borane hydrogen atoms;[2a] on the contrary, uranium in principle can provide energetically suitable 5*f* orbitals for such co-ordination, in addition to the 7*s* and 6*d*. This hypothesis concerning the participation of the *f* orbitals in the bonding in uranium compounds is increasingly supported by the unique organometallic chemistry of uranium compared to that of *d* transition metals.[15]

Acknowledgements

The authors thank Professor R. D. Fischer for helpful discussion and Mr. F. Braga and Mr. V. Corrado for skilful technical assistance.

References

1 D. Mannig and H. Nöth, *J. Organomet. Chem.*, 1984, **275**, 169; V. D. Sasnovskaya, L. V. Titov, and V. Ya. Rosolovskii, *Bull. Acad. Sci. USSR*, 1984, **33**, 1297.
2 (*a*) J. A. Marsella and K. G. Caulton, *J. Am. Chem. Soc.*, 1982, **104**, 2361; (*b*) L. H. Long, *Adv. Inorg. Chem. Radiochem.*, 1973, **16**, 20.
3 H. Nöth and M. Seitz, *J. Chem. Soc., Chem. Commun.*, 1976, 1004.
4 K. C. Nainan and G. E. Ryschkewitsch, *Inorg. Nucl. Chem. Lett.*, 1970, **6**, 765.
5 J. A. van Doorn, C. Masters, and H. C. Volger, *J. Organomet. Chem.*, 1976, **105**, 245.
6 G. Rossetto, M. Porchia, F. Ossola, P. Zanella, and R. D. Fischer, *J. Chem. Soc., Chem. Commun.*, 1985, 1460.
7 (*a*) T. J. Marks and R. D. Ernst, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford, 1982, vol. 3, ch. 21 and refs. therein; (*b*) G. Paolucci, G. Rossetto, P. Zanella, K. Yünlü, and R. D. Fischer, *J. Organomet. Chem.*, 1984, **272**, 363; (*c*) F. Ossola, N. Brianese, M. Porchia, G. Rossetto, P. Zanella, and R. D. Fischer, 12th Int. Conf. Organomet. Chem., Vienna, 1985.
8 E. R. Birnbaum and P. H. Javora, *J. Organomet. Chem.*, 1967, **9**, 379.
9 T. J. Marks and J. R. Kolb, *J. Am. Chem. Soc.*, 1975, **97**, 27.
10 D. J. Pasto, V. Balasubramaniyan, and P. W. Wojtkowski, *Inorg. Chem.*, 1969, **8**, 595.
11 J. E. Huheey, 'Inorganic Chemistry; Principles of Structure and Reactivity,' Harper and Row, New York, 1972, appendix f, table F1.
12 H. C. Brown, A. Tsukamoto, and D. B. Bigley, *J. Am. Chem. Soc.*, 1960, **82**, 4703.
13 J. L. Hubbard and K. Smith, *J. Organomet. Chem.*, 1984, **276**, C41.
14 Ref. 12, ch. 6.
15 R. E. Cramer, K. Panchanatheswaran, and J. W. Gilje, *J. Am. Chem. Soc.*, 1984, **106**, 1853.

Received 18*th February* 1986; *Paper* 6/340