

**SYNTHESIS AND SOME REACTIONS OF THE STABLE CARBOCATIONS
STABILIZED BY THE 1-[*closo*-3,3,3-(CO)₃-3,1,2-ReC₂B₉H₁₀]⁻ GROUP.
THE STRUCTURE OF *closo*-3,3,3-(CO)₃-3,1,2-ReC₂B₉H₁₀⁻-1- $\dot{\text{C}}$ Me₂ ***

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Summary

The stable carbenium cations in the zwitterionic complexes *closo*-3,3,3-(CO)₃-3,1,2-ReC₂B₉H₁₀⁻-1- $\dot{\text{C}}$ RR' (R = R' = H; R = H, R' = Me; R = R' = Me) have been prepared by protonation of *closo*-3,3,3-(CO)₃-3,1,2-ReC₂B₉H₁₀⁻-1-CH₂OR (R = H, Me) and *closo*-3,3,3-(CO)₃-3,1,2-ReC₂B₉H₁₀⁻-1-CR=CH₂ (R = H, Me). Some of the reactions of the zwitterions with neutral and charged nucleophilic reagents have been studied. The crystal and molecular structure of *closo*-3,3,3-(CO)₃-3,1,2-ReC₂B₉H₁₀⁻-1- $\dot{\text{C}}$ Me₂ has been established. It is shown that the carbocationic centre in these zwitterions is stabilized by direct Re-C interaction.

Introduction

Studies of α -ferrocenylcarbocations carried out as early as 1959 [1] have proved that π -complexes of transition metals are among some of the most effective neighbouring groups to stabilize the carbocationic centre. Later, a series of carbenium ions stabilized by ruthenium, osmium, chromium, manganese, cobalt and iron π -complexes were obtained [2,3]. We have recently shown that the 1- π -cyclopentadienyl- π -(3)-1,2-dicarbollyliron(II) group, 1-[π -C₅H₅Fe^{II}-(3)- π -1,2-C₂B₉H₁₀]⁻ is capable of stabilizing the α -carbocationic centre in the same way as the isoelectronic ferrocenyl group π -C₅H₅FeC₅H₄⁻, and we have obtained a number of stable carbocations, π -C₅H₅Fe^{II}-(3)-1,2-C₂B₉H₁₀⁻-1- $\dot{\text{C}}$ RR', which can be formally considered as zwitterions, with the positive charge on the exopolyhedral carbocationic centre and the negative charge on the 1-[π -C₅H₅Fe^{II}-(3)- π -1,2-C₂B₉H₁₀]⁻ group [4,5]. An X-ray study of zwitterionic π -C₅H₅Fe^{II}-(3)- π -1,2-C₂B₉H₁₀⁻-1- $\dot{\text{C}}$ HC₆H₅ has

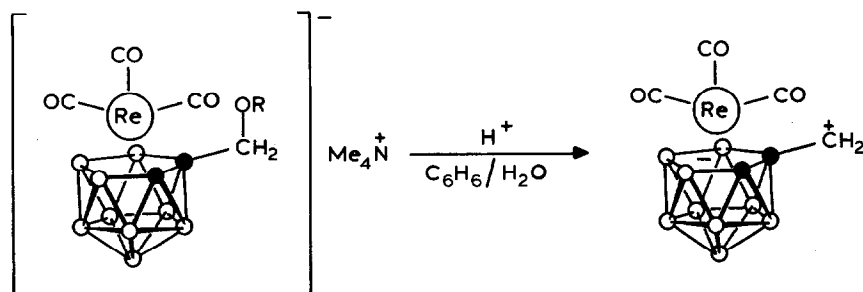
* Dedicated to Academician O.A. Reutov on the occasion of his 65th birthday.

shown that stabilization of the carbocationic centre is due to its direct interaction with the iron atom, this interaction, as can be inferred from the molecular geometry, being considerably greater than that in analogous α -ferrocenylcarbocations [5].

On the basis of kinetic data it was suggested previously that $(\text{CO})_3\text{MnC}_5\text{H}_4$ and $(\text{CO})_3\text{ReC}_5\text{H}_4$ groups should have the same stabilizing effect on the α -carbocationic centre [6]. However, carbenium ions stabilized by the $(\text{CO})_3\text{ReC}_5\text{H}_4$ group have not yet been obtained. Taking into account the results published previously [5], we suggest that the 1-[*closo*-3,3,3-(CO)₃-3,1,2-ReC₂B₉H₁₀]⁻ group should be able to stabilize the α -carbocationic centre considerably. In the present paper this assumption is shown to be correct, and new stable carbocations stabilized by the 1-[*closo*-3,3,3-(CO)₃-3,1,2-ReC₂B₉H₁₀]⁻ group are reported.

Results and discussion

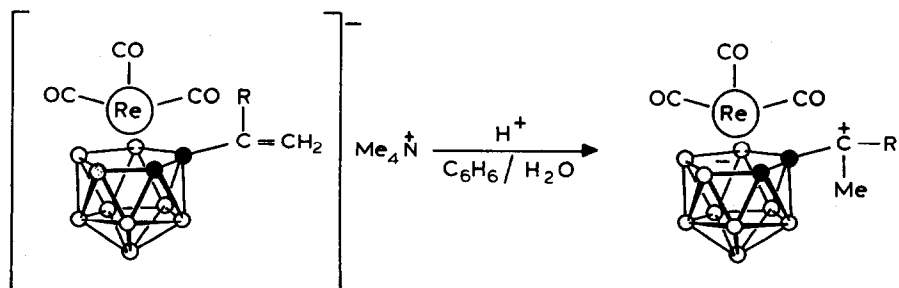
It has been found that protonation of the tetramethylammonium salt of *closo*-ROCH₂-3,3,3-(CO)₃-3,1,2-ReC₂B₉H₁₀ (Ia, R = H, Ib, R = Me) by 40% HBF₄ or 35% H₂SO₄ in C₆H₆/H₂O results in stable primary carbocations incorporated in the zwitterionic molecule of *closo*-1- $\dot{\text{C}}\text{H}_2$ -3,3,3-(CO)₃-3,1,2-ReC₂B₉H₁₀ (II).



(Ia, R = H;
Ib, R = Me)

● — C or CH
O — BH

Complex II was isolated as light-yellow crystals. It is air-stable both in the crystalline state and in solution. Protonation of the tetramethylammonium salts of *closo*-1-CH₂=CH-3,3,3-(CO)₃-3,1,2-ReC₂B₉H₁₀ (III) and *closo*-1-CH₂=C(Me)-3,3,3-(CO)₃-3,1,2-ReC₂B₉H₁₀ (IV) under similar conditions also gives zwitterionic complexes V and VI, respectively, with the secondary (V) and tertiary (VI) carbocationic centres:



(III, R = H;
IV, R = Me)

● — C or CH
O — BH

(V, R = H;
VI, R = Me)

Zwitterions V and VI are light-yellow, crystalline substances. Similar to complex II with the primary carbocationic centre, they are air-stable in the crystalline state and in solution. Complex V is a mixture of two diastereomers which can easily be separated by TLC. The ability of carbocation V to form diastereomers is due to the presence of two asymmetric centres: the chiral π -dicarbollyl ligand and the cationic carbon atom coordinated by the rhenium atom. In the zwitterionic compounds II, V and VI, the positive charge on the exopolyhedral carbon atom is compensated by the negative charge of the π -dicarbollyl ligand so that the molecules II, V and VI, as a whole, are electroneutral. We call these types of carbenium derivatives "carbenium zwitterions" [5].

The ^1H and ^{13}C NMR spectra of carbenium zwitterions II, V and VI were measured (Tables 1 and 2). The ^1H and ^{13}C NMR spectral data indicate magnetic non-equivalence of the hydrogen atoms in II and the CH_3 groups in VI bonded to the carbocationic centre. This is indicative of hindered rotation around the $\text{C}_{\text{carb.}}-\text{C}_{\text{exo}}^+$ bond, which is probably due to the direct interaction $\text{Re}-\text{C}_{\text{exo}}^+$ and the partial double bond character of the $\text{C}_{\text{carb.}}-\text{C}_{\text{exo}}^+$ bond. The $J(\text{CH}(\text{exo}))$ value of 170 Hz for the

TABLE 1

^1H NMR SPECTRAL DATA OF SOME COMPOUNDS WITH A CARBOCATIONIC CENTRE IN THE MOLECULE

Compound	δ (ppm) ^a	J (Hz)	Assignment	Reference
$\text{Re}(\text{CO})_3\text{Cb}\dot{\text{C}}\text{H}_2$ (II) ^b	1.68d	2.55	CH_2	This work
	2.37d	2.55	$\dot{\text{C}}\text{H}_2$	
	2.02s		CH carbor.	
$\text{Re}(\text{CO})_3\text{Cb}\dot{\text{C}}\text{HCH}_3$ (V)	0.68d	6.35	CH_3	This work
	1.06d	6.35	CH_3	
	1.57s		CH carbor.	
	2.38q	6.35	$\dot{\text{C}}\text{H}$	
	2.46s		CH carbor.	
	2.96	6.35	CH	
$\text{Re}(\text{CO})_3\text{Cb}\dot{\text{C}}\begin{smallmatrix} \text{CH}_3 \\ \diagup \\ \text{CH}_3 \end{smallmatrix}$ (VI)	0.89s		CH_3	This work
	1.25s		CH_3	
	2.28		CH carbor.	
$\text{Fc}\dot{\text{C}}\text{H}_2$	4.05		CH_2	[7]
FcCHCH_3	2.88q		CH	[7]
	7.55d		CH_3	
$\text{Fc}\dot{\text{C}}\begin{smallmatrix} \text{CH}_3 \\ \diagup \\ \text{CH}_3 \end{smallmatrix}$	7.77s		2CH_3	[7]
$\text{Cm}\dot{\text{C}}\text{HC}_6\text{H}_5$	2.60		$\dot{\text{C}}\text{H}$	[8]
$\text{CpCbFe}\dot{\text{C}}\text{H}_2$	0.94s		CH carbor.	[5]
	3.02s		$\dot{\text{C}}\text{H}_2$	
	3.49s		$\dot{\text{C}}\text{H}_2$	
$\text{CpCbFe}\dot{\text{C}}\text{HCH}_3$	4.27q		$\dot{\text{C}}\text{H}$	
	1.05d		CH_3	
	1.78s		CH carbor.	

^a Relative to TMS. ^b Cb = 1, 2- $\text{C}_2\text{B}_9\text{H}_{10}^-$.

CH_2 group in cation II is also in agreement with sp^2 - rather than sp^3 -hybridization of the C_{exo} atom. The values of the chemical shifts of the $\dot{\text{C}}_{exo}^+$ atoms in the ^{13}C NMR spectra of zwitterions II, V and VI show that the $\dot{\text{C}}_{exo}^+$ atoms in these zwitterions are more shielded than those in the corresponding ferrocenyl carbocations [7], cymantrenyl carbocation $\text{Cm}\dot{\text{C}}\text{HPh}$ [8] and tolylchrometricarbonyl carbocation $(\text{CO})_3\text{CrCH}_3\text{C}_6\text{H}_4\dot{\text{C}}\text{HCH}_3$ [9] (Table 2). Comparison of the chemical shifts in the ^{13}C NMR spectra of the $\dot{\text{C}}_{exo}$ atoms in II and in $\text{CpFe}^{\text{II}}\text{HCB}_9\text{H}_9\dot{\text{C}}\text{CH}_2$ [10] indicates that the $\dot{\text{C}}_{exo}$ atom is more shielded in the former compound than in the latter. Since the charge density at the carbocationic centre is the main factor determining the shielding of the carbon atom nucleus [2], the results of the ^{13}C NMR study suggest considerable delocalization of the positive charge in molecules II, V and VI. The high stability of these compounds is undoubtedly due to this fact. Comparison of the chemical shifts of the C_{exo} atoms in II, V and VI shows that delocalization of the positive charge increases in the sequence primary < secondary < tertiary, similar to the sequence in the corresponding ferrocenyl carbocations [7]. Participation of the π -dicarbollyl ligand in the delocalization of the positive charge

TABLE 2

^{13}C NMR SPECTRAL DATA OF SOME COMPOUNDS WITH A CARBOCATIONIC CENTRE IN THE MOLECULE

Compound	Chemical shift ^a $\delta(\text{ppm})$	Assignment	Reference
$\text{Re}(\text{CO})_3\text{Cb}\dot{\text{C}}\text{H}_2$ (II) ^b	$\left\{ \begin{array}{l} 32.27 \\ 58.75 \\ 94.42 \end{array} \right.$	$\begin{array}{l} \text{CH}_2 \\ \text{CH carbor.} \\ \text{CH carbor.} \end{array}$	This work
$\text{Re}(\text{CO})_3\text{Cb}\dot{\text{C}}\text{HCH}_3$ (V)	$\left\{ \begin{array}{l} 29.31 \\ 32.18 \\ 52.89 \\ 53.95 \\ 56.62 \\ 57.80 \\ 94.27 \\ 98.98 \end{array} \right.$	$\begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \\ \dot{\text{C}}\text{H} \\ \text{CH carbor.} \\ \dot{\text{C}}\text{H} \\ \text{CH carbor.} \\ \text{C carbor.} \\ \text{C carbor.} \end{array}$	This work
$\text{Re}(\text{CO})_3\text{Cb}\dot{\text{C}}\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C} \\ \diagdown \\ \text{CH}_3 \end{array}$ (VI)	$\left\{ \begin{array}{l} 27.65 \\ 28.31 \\ 54.93 \\ 79.08 \\ 98.20 \end{array} \right.$	$\begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH carbor.} \\ \dot{\text{C}} \\ \text{C carbor.} \end{array}$	This work
$\text{Fc}\dot{\text{C}}\text{H}_2$	88.6	$\dot{\text{C}}\text{H}_2$	[7]
$\text{Fc}\dot{\text{C}}\text{HCH}_3$	119.5	$\dot{\text{C}}\text{H}$	[7]
$\text{Fc}\dot{\text{C}}\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C} \\ \diagdown \\ \text{CH}_3 \end{array}$	158.6	$\dot{\text{C}}$	[7]
$\text{Cm}\dot{\text{C}}\text{HC}_6\text{H}_5$	144.5	$\dot{\text{C}}\text{H}$	[8]
$(\text{CO})_3\text{CrC}_6\text{H}_4(\text{CH}_3)\dot{\text{C}}\text{HCH}_3$	126.6	$\dot{\text{C}}\text{H}$	[9]

^a Relative to TMS. ^b Cb = 1, 2- $\text{C}_2\text{B}_9\text{H}_{10}^-$.

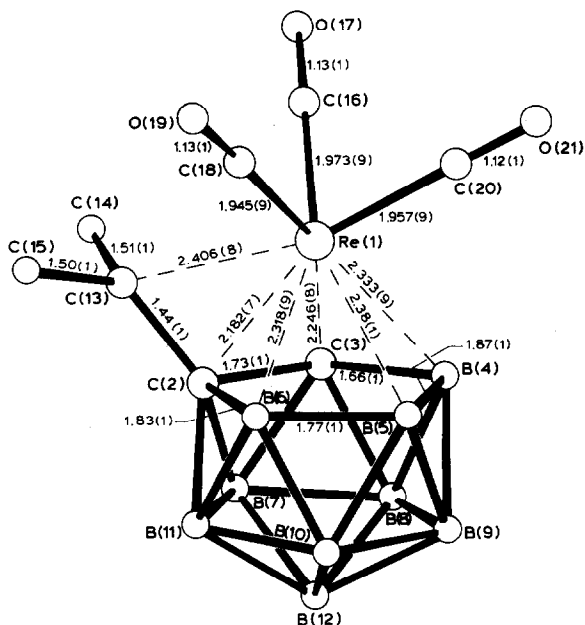


Fig. 1. Structure of molecule VI.

is indicated by the ^{13}C chemical shifts of the C_{carb} atoms bonded to C_{exo} : they are equal to 94–99 ppm in II, V and VI, while the ^{13}C chemical shifts of the C_{carb} atom bonded to the CH_2OCH_3 group are equal to 81.9 ppm, i.e. when II is formed from Ib, considerable deshielding of the C_{carb} atom takes place.

In the ^{13}C NMR spectrum of carbocation II, the non-equivalence of the CO groups which have chemical shifts at 186.74, 187.16 and 188.43 ppm is clearly observed. This means that rotation of the $\text{Re}(\text{CO})_3$ group relative to the $\text{Re}-\pi$ -dicarbollyl ligand is hindered because of the formation of the bond between the rhenium atom and the carbocationic centre.

Useful information on the structure and probable mechanism of stabilization of the carbenium zwitterions was obtained through X-ray analysis of complex VI. The crystals of VI are orthorhombic, at $+20^\circ\text{C}$, a 9.3101(5), b 12.696(1), c 12.9871(6) Å, V 1535.1(2) Å³, d_{calc} 1.920 g cm⁻³, Z = 4, space group $P2_12_12_1$. The structure of molecule VI is shown in Fig. 1. The bond lengths and main bond angles are listed in Tables 3 and 4, respectively.

The geometry of the metal atom coordination by the π -dicarbollyl ligand in VI is similar to that observed in $\pi\text{-C}_5\text{H}_5\text{-Fe}^{\text{II}}\text{-(3)-1,2-C}_2\text{B}_3\text{H}_{10}\text{-1-}\dot{\text{C}}\text{HC}_6\text{H}_5$ (VII) [5]. The Re atom is not only coordinated by the five atoms of the open C_2B_3 plane of the dicarbollyl ligand but is also bonded to the exopolyhedral carbenium atom (C_{exo} , C(13) atom in Fig. 1). A number of bonding patterns in complex VII, most of which suggest direct interaction between the metal atom and the exopolyhedral carbocationic centre, were given in [5]. As in the case of molecule VII, the geometrical parameters of molecule VI confirm the existence of such an interaction. It is indicated by the considerable shift of the Re atom relative to the centre of the C_2B_3 plane towards the C_{exo} atom which results in a short $\text{Re}-\text{C}_{\text{exo}}$ distance (2.406(8) Å)

TABLE 3
BOND LENGTHS d (Å) IN VI

Bond	d	Bond	d	Bond	d
Re(1)–C(2)	2.182(7)	C(3)–B(4)	1.66(1)	B(7)–B(12)	1.77(2)
Re(1)–C(3)	2.246(8)	C(3)–B(7)	1.74(1)	B(8)–B(9)	1.78(2)
Re(1)–B(4)	2.333(9)	C(3)–B(8)	1.73(1)	B(8)–B(12)	1.77(2)
Re(1)–B(5)	2.38 (1)	B(4)–B(5)	1.87(1)	B(9)–B(10)	1.76(2)
Re(1)–B(6)	2.318(9)	B(4)–B(8)	1.84(1)	B(9)–B(12)	1.82(2)
Re(1)–C(13)	2.406(8)	B(4)–B(9)	1.84(1)	B(10)–B(11)	1.77(2)
Re(1)–C(16)	1.973(9)	B(5)–B(6)	1.77(1)	B(10)–B(12)	1.75(2)
Re(1)–C(18)	1.945(9)	B(5)–B(9)	1.83(1)	B(11)–B(12)	1.80(2)
Re(1)–C(20)	1.957(9)	B(5)–B(10)	1.83(1)	C(13)–C(14)	1.51(1)
C(2)–C(3)	1.73 (1)	B(6)–B(10)	1.78(1)	C(13)–C(15)	1.50(1)
C(2)–B(6)	1.83(1)	B(6)–B(11)	1.82(1)	C(16)–O(17)	1.13(1)
C(2)–B(7)	1.72(1)	B(7)–B(8)	1.83(1)	C(18)–O(19)	1.13(1)
C(2)–B(11)	1.72(1)	B(7)–B(11)	1.83(2)	C(20)–O(21)	1.12(1)
C(2)–C(13)	1.44(1)				

and significant differences in the Re–C and Re–B distances involving the B and C atoms of the C_2B_3 open face. Asymmetric coordination of the metal by the π -dicarbollyl ligand is clearly seen in Fig. 2, which shows the projections of the coordination sphere of the Re atom upon the C_2B_3 plane of molecule VI and rheniumcarborane anion $[3,3,3-(CO)_3-3,1,2-ReC_2B_9H_{11}]^-$ (VIII), which was structurally studied in the form of its cesium salt [11]. In principle, the Re–C_{exo} interaction in VI can be considered as an ordinary metal–carbon σ -bond, although such an interaction does not explain the number of geometrical peculiarities of zwitterion VI. In fact, on the one hand, the Re–C_{exo} distance considerably exceeds the sum (2.28 Å) of the covalent radii of the Re atom (1.51 Å) [12] and the sp^3 -hybridized C atom (0.77 Å) [13], as well as the Re–C_{sp} bond lengths found in a number of rhenium complexes, for instance, 2.31 Å in $CH_3Re(CO)_5$ [14]. On the other hand, the short C_{carb}–C_{exo} bond (C(2)–C(13) 1.44(1) Å) and considerably widened (in comparison with the tetrahedral value) bond angles (C(2)C(13)C(14) 120.2(7)°, C(2)C(13)C(15) 120.2(7)° and C(14)C(13)C(15) 112.3(8)° are in better agreement with sp^2 - rather

TABLE 4
MAIN BOND ANGLES ω (°) IN VI

Angle	ω	Angle	ω	Angle	ω
C(16)Re(1)B(5)	152.4(3)	Re(1)C(2)B(6)	70.0(4)	C(2)B(6)B(5)	104.3(6)
C(16)Re(1)B(6)	155.9(3)	Re(1)C(2)C(13)	80.3(5)	Re(1)C(13)C(2)	64.4(4)
C(18)Re(1)C(3)	154.4(3)	C(3)C(2)B(6)	109.0(5)	Re(1)C(13)C(14)	115.4(6)
C(18)Re(1)B(4)	153.1(3)	C(3)C(2)C(13)	112.2(6)	Re(1)C(13)C(15)	116.8(6)
C(20)Re(1)C(2)	158.3(3)	B(6)C(2)C(13)	114.6(6)	C(2)C(13)C(14)	120.2(7)
C(20)Re(1)C(13)	165.4(4)	B(7)C(2)C(13)	129.6(7)	C(2)C(13)C(15)	120.2(7)
C(16)Re(1)C(18)	95.5(3)	B(11)C(2)C(13)	135.0(7)	C(14)C(13)C(15)	112.3(8)
C(16)Re(1)C(20)	85.2(4)	C(2)C(3)B(4)	111.8(6)	Re(1)C(16)O(17)	176.5(7)
C(18)Re(1)C(20)	84.1(4)	C(3)B(4)B(5)	106.6(7)	Re(1)C(18)O(19)	177.3(8)
Re(1)C(2)C(3)	68.9(4)	B(4)B(5)B(6)	108.2(7)	Re(1)C(20)O(21)	178.2(8)

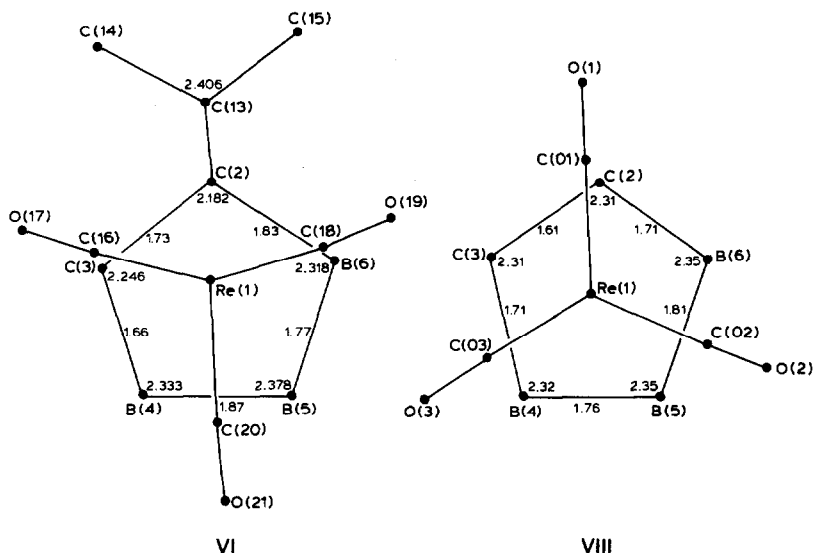


Fig. 2. Projection of the coordination environment of the Re atom in molecules VI and VIII on the plane of the C_2B_3 face of the carborane ligand. The distance from the Re atom is shown beside each atom of the C_2B_3 face and the C(13) atom.

than sp^3 -hybridization of the C_{exo} atom. These results, as well as the ^{13}C NMR data, indicate the significant double bonding between the C(2) and C(13) atoms and allow carbocation VI to be considered as a "pseudo-fulvene" π complex which appears to be a carboranyl analogue of fulvene π complexes where the metal atom is coordinated by two bonds involved in the five-membered ring and one exocyclic double bond of the fulvene ligand (e.g. [15]). In terms of this interpretation it would be interesting to compare the bond lengths in the C_2B_3 plane in complexes VI and VIII coordinating the rhenium atom. As can be seen from Fig. 2, in the carborane polyhedron of molecule VI the C(3)–B(4) and B(5)–B(6) edges are markedly shorter, while the C(2)–C(3), C(2)–B(6) and B(4)–B(5) edges are considerably longer than the corresponding bonds in the C_2B_3 plane of molecule VIII. The distances C(2)–C(3) (1.73(1) Å) and C(2)–B(6) (1.83(1) Å) are among the longest C–C and C–B bonds observed earlier in the structures of icosahedral metallocarboranes [16]. If one also takes into account the shortening of the C(2)–C(13) bond in VI indicating its partially double bond character then we arrive at the fulvene-type bond system. It should be noted that analogous redistribution of the bond lengths in the five-membered ring coordinating the iron atom of the C_2B_3 plane of the carborane ligand was also found in molecule VII [5]. However, in the present structure VI (evidently due to its higher accuracy) this tendency is much more pronounced.

It is worth noting that the $M-C_{exo}$ interaction in both metallocarborane complexes VI and VII appears to be somewhat stronger than that in complexes with conventional carbon fulvene ligands, such as $[CpFe(C_5H_4CPh_2)]^+ BF_4^-$ (IX) [17] and $(CO)_3Cr(C_5H_4CPh_2)$ (X) [18]. In fact, the distances $Fe-C_{exo}$ in VII (2.23 Å) and $Re-C_{exo}$ in VI exceed the corresponding sums of the covalent radii by only 0.1 Å, while in IX and a number of analogous ferrocenylcarbenium complexes [17,19,20] this difference amounts to 0.6–0.7 Å; in the derivative of chromium (X) it is equal to

0.3 Å [18]. The more significant $M-C_{exo}$ interaction in complexes VI and VII is probably due to more favourable geometrical conditions for coordination. In the non-coordinated fulvene molecule, the exocyclic C atom is in the plane of the five-membered ring and its approach to the metal atom upon coordination requires a certain amount of additional energy necessary for the distortion of the planarity of the system (in complexes IX and X the $C_{cycl}-C_{exo}$ bonds form angles of 20.7° and 28.9°, respectively, with the C_2B_3 plane). At the same time, in the non-coordinated *nido*-carborane ligand, the exopolyhedral $C_{carb}-C_{exo}$ bond is inclined by $\sim 25^\circ$ and the C_{exo} atom is displaced from this plane towards the missing vertex of the icosahedron. It is natural that an additional tilt of this bond towards the metal atom upon its coordination equal to $\sim 25^\circ$, as in the case of fulvene complexes (inclination of the $C_{carb}-C_{exo}$ bond to the C_2B_3 plane observed in VII and VI is equal to 47° and 47.9°, respectively), allows the significantly closer approach of the C_{exo} atom to the metal atom in metallocarboranes.

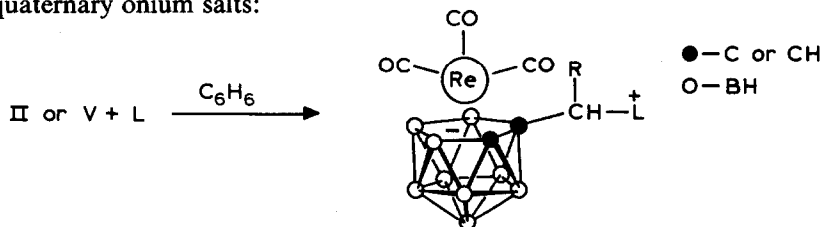
Considering the substituted carborane ligand in VI as pseudo-fulvene, one may describe the coordination environment of the Re atom in this complex as a distorted octahedron with carbonyl groups positioned *trans* to each of the "fulvene double" bonds C(3)–B(4), B(5)–B(6) and C(2)–C(13). A very similar orientation of the $M(CO)_3$ group, and therefore an analogous type of metal atom coordination, was previously observed in the chromium fulvene complex X [18]. In molecule VI, the bond angles at the metal atom in the $M(CO)_3$ group differ significantly from each other. The increase of the angle C(16)Re(1)C(18) to 95.5(3)° and the decrease of angles C(16)Re(1)C(20) to 85.2(4)° and C(18)Re(1)C(20) to 84.1(4)° are due to the repulsion of the carbonyl groups C(16)O(17) and C(18)O(19) from the C(13) atom and the C(14) and C(15) Me groups: the corresponding non-bonding distances are equal to C(13)···C(16) 2.96(1), C(13)···C(18) 3.00(1), C(14)···C(16) 2.99(1), C(15)···C(18) 3.06(1) Å, i.e. they are considerably less than the double Van der Waals radius of the carbon atom (3.4 Å [13]).

The Re–C(CO) bond lengths 1.945(9), 1.957(9) and 1.973(9) Å and the C–O bond lengths 1.13(1), 1.12(1) and 1.13(1) Å in molecule VI are respectively longer and shorter than those in molecule VIII (mean values for Re–C and C–O are 1.89 and 1.16 Å). The Re–C(CO) distances are also greater than those found in most cyclopentadienylrhenium complexes, in which the Re–C(CO) bond lengths are equal to 1.85–1.90 Å [21]. At the same time, in complexes which do not contain Cp ligands similar to those observed in VI even longer Re–C(CO) distances were found (for example, 2.000–2.010 Å in $H_3XRe(CO)_5$; X = C, Si, Ge [14]).

This peculiarity of the cyclopentadienylcarbonyl complexes is probably due to the strong π -donating properties of the Cp ligand which enhance back-donation and hence lead to strengthening of the Re–C(CO) bonds. Taking into consideration the Re–C(CO) bond lengths observed in VI, one can come to the conclusion that the substituted carborane ligand in the present complex has a somewhat weaker π -donating effect than the cyclopentadienyl ligand.

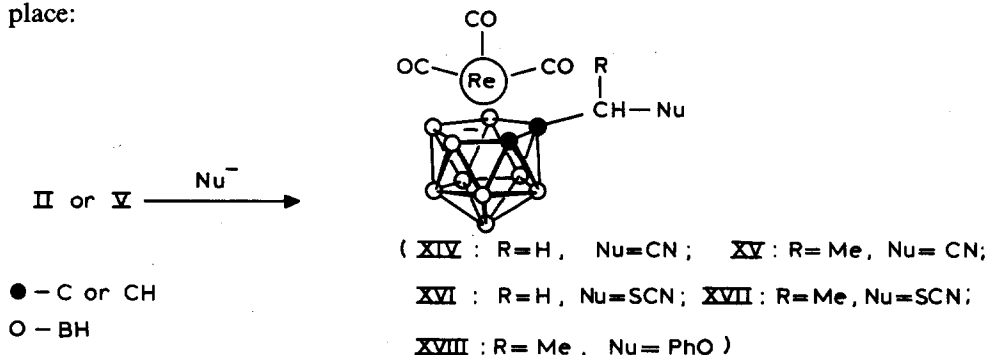
Although compounds II, V and VI should be most adequately treated as "pseudo-fulvene complexes" in which the positive charge on the carbocationic centre is strongly delocalized, they still retain the ability to take part in reactions involving nucleophilic attack at the carbocationic centre, viz. in reactions with neutral Lewis bases and with charged nucleophilic reagents. However, the carbenium zwitterions II, V and VI were found to be considerably less reactive than the

corresponding α -ferrocenylcarbenium ions and even carbenium ions of the π - $C_5H_5Fe^{II}-(3)-\pi-1,2-C_2B_9H_{10}-1-\dot{C}RR'$ type, where $R = H, Me, Ph$. Thus, II and V react slowly with pyridine and triphenylphosphine to yield the corresponding inner quaternary onium salts:

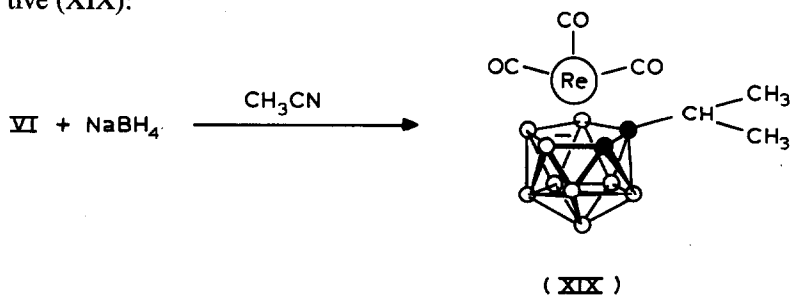


(**XI**, $R = H$, $L = C_5H_5N$;
XIII, $R = Me$, $L = Ph_3P$)
 (**XII**, $R = Me$; $L = C_5H_5N$)

Unlike II and V, cation VI does not form a quaternary salt upon interaction with pyridine. In this case, one of the Me-group protons is eliminated and the isopropenyl derivative (IV) is formed. When nucleophilic reagents such as NaCN, KSCN, PhONa react with II and V, nucleophilic addition of these nucleophiles at the carbocationic centre with the formation of the corresponding anionic adducts takes place:



The reaction of cation VI with NaCN also results only in the abstraction of the Me-group proton and the formation of anion IV. It is assumed that the absence of addition products to the carbocationic centre of zwitterion VI upon interaction with pyridine and NaCN is to a considerable degree due to the presence of bulky substituents effectively shielding the carbocationic centre. Thus, zwitterion VI reacts smoothly with smaller-sized nucleophiles, e.g. $NaBH_4$, to yield the isopropyl derivative (**XIX**):



The reaction of NaBH_4 and cation V also proceeds readily and results in the ethyl derivative *closo*-3,3,3-(CO)₃-3,1,2-ReC₂B₉H₁₀-1-Et (XX).

Studies of the reactions of zwitterions II and V with a number of nucleophilic reagents have shown that the reactions of these carbocations with nucleophilic reagents can be used as a convenient procedure for preparing various derivatives of tricarbonylrheniumdicarbollyl substituted at the carborane C atom.

Experimental

Reagents and materials

Syntheses of compounds Ia, Ib, III and IV were carried out in an atmosphere of dry argon; absolute solvents were used. THF and ether were purified by distillation over LiAlH_4 . MeCN was distilled over CaH_2 . Column chromatography was performed on Chemapol silica gel (100/160). Silufol plates were used for TLC.

Apparatus

IR spectra were measured on a UR-10 spectrometer (in KBr pellets or in hexachlorobutadiene). ^1H and ^{13}C NMR spectra were recorded on a Bruker WP-200SY instrument. The cell parameters and intensities of 1912 observed reflections ($F^2 \geq 3\sigma$) were measured at $+20^\circ\text{C}$ with an automatic four-circle Hilger and Watts diffractometer (Mo- K_α radiation, graphite monochromator, $\theta/2\theta$ scan, $\theta \leq 30^\circ$). The structure was solved by the heavy atom method. The Re atom coordinates were determined from Patterson synthesis; other non-hydrogen atoms were located in the subsequent electron density and difference Fourier syntheses. After refinement of the structure by the least-squares technique in the isotropic approximation, the experimental intensities were corrected for absorption according to the technique described in [22], resulting in a significant decrease of the *R* factor (from 0.0971 to 0.0472). Then the structure was refined by full matrix least-squares in the anisotropic approximation; only one-third of the hydrogen atoms was located in the difference Fourier synthesis and therefore hydrogen atoms were not included in further structure refinement.

The absolute configuration of the molecule was determined by means of the Hamilton test based on the refinement of both the direct and inverted structures, taking into account the anomalous scattering by the Re and O atoms. The difference in the final discrepancy factors ($R = 0.0253$, $R_w = 0.0309$ for the direct; $R = 0.0335$, $R_w = 0.0434$ for the inverted structures) corresponded to a 99.5% probability of the correct assignment of the absolute determination. All calculations were performed with an Eclipse S/200 computer using INEXTL programs [23]. The atomic coordinates are given in Table 5.

[*closo*-3,3,3-(CO)₃-ReC₂B₉H₁₀-1-CH₂OMe][−]Me₄N⁺ (Ib)

0.82 g (3.7 mmol) of $\text{Na}_2[1\text{-CH}_3\text{OCH}_2\text{-1,2-C}_2\text{B}_9\text{H}_{10}]^-$ [24] in 20 ml THF was added dropwise to a solution of 1.5 g (3.7 mmol) of BrRe(CO)_5 in 100 ml of THF. The mixture was refluxed for 60 h, cooled, and the solvent was evaporated. The precipitate was dispersed in 20 ml of water, filtered, and the mother liquor was treated with excess aqueous solution of Me_4NBr . The cream-coloured residue was separated, washed with water, and dried in vacuo over P_2O_5 . 0.85 g (44%) was obtained. Found: C, 25.47; H, 5.48; B, 18.13; Re, 36.06. $\text{C}_{11}\text{H}_{27}\text{B}_9\text{NO}_4\text{Re}$ calcd.: C,

TABLE 5
 ATOMIC COORDINATES ($\times 10^4$; for Re, $\times 10^5$) AND TEMPERATURE FACTORS

Atom	x	y	z	$B_{\text{iso}}^{\text{eq}}$	Atom	x	y	z	$B_{\text{iso}}^{\text{eq}}$
Re(1)	23730(3)	21269(2)	14028(2)	2.27(1)	B(12)	-138(14)	1580(9)	3992(9)	4.3(3)
C(2)	2367(8)	2275(5)	3077(5)	2.4(1)	C(13)	3725(9)	2772(8)	2850(6)	2.9(2)
C(3)	931(8)	2946(8)	2535(6)	2.7(2)	C(14)	3872(11)	3952(7)	2913(7)	3.7(2)
B(4)	-68(10)	2165(8)	1806(7)	3.0(2)	C(15)	5107(8)	2216(10)	3089(7)	4.0(2)
B(5)	708(11)	810(8)	1925(8)	3.3(2)	C(16)	2859(8)	3494(7)	771(6)	3.2(2)
B(6)	2260(10)	886(7)	2710(6)	2.9(2)	O(17)	3100(7)	4302(5)	447(5)	4.7(2)
B(7)	985(11)	2698(8)	3850(7)	3.2(2)	C(18)	4128(9)	1420(7)	977(6)	3.3(2)
B(8)	-665(11)	2558(9)	3098(9)	3.7(3)	O(19)	5165(7)	1009(6)	769(6)	4.9(2)
B(9)	-818(11)	1214(9)	2726(8)	3.6(3)	C(20)	1691(11)	1740(7)	28(6)	3.8(2)
B(10)	614(13)	525(9)	3306(8)	4.1(3)	O(21)	1304(8)	1492(7)	-753(5)	5.5(2)
B(11)	1775(13)	1382(9)	3982(7)	3.7(2)					

25.37; H, 5.22; B, 18.68; Re, 35.75%. IR spectrum: 1910, 2020 (CO), 2400–2600 (BH), 2820–2960 (CH₃, CH₂), 3040 cm⁻¹ (carborane CH).

[closo-3,3,3-(CO)₃-ReC₂B₉H₁₀-1-CH₂OH] Me₄N (Ia)

A mixture of 3.26 g (8.03 mmol) of BrRe(CO)₅ and 4.59 g (8.03 mmol) of Ti₂[1-OHCH₂-1,2-C₂B₉H₁₀] in 150 ml THF was boiled for 30 h. After cooling, the mixture was filtered, the precipitate was washed with THF, the filtrate obtained was treated with an excess of NaI · 2H₂O and then evaporated to dryness in vacuo. The residue was dispersed in water and filtered off. The filtrate was treated with an excess aqueous Me₄NBr. The residue obtained was separated, washed with water, and dried in vacuo over P₂O₅. 2.16 g was obtained. According to elemental analysis, the product contained 86% of Me₄N[3,3,3-(CO)₃-ReC₂B₉H₁₀-1-CH₂OH] and 14% of Me₄NI. IR spectrum: 3560 (free OH), 3300–3650 (bound OH), 3040 (carborane CH), 2510–2550 (BH); 2020–1900 cm⁻¹ (CO).

[closo-3,3,3-(CO)₃-ReC₂B₉H₁₀-1-CH=CH₂] Me₄N (III)

9.44 mmol (62.9 ml of 0.15 M solution) of Na₂[1-CH₂=CH-1,2-C₂B₉H₁₀] was added to 3.83 g (9.44 mmol) of BrRe(CO)₅ in 75 ml of THF and refluxed for 20 h. Then the reaction mixture was filtered and the precipitate was washed with THF (2 × 25 ml). The combined filtrates were evaporated to dryness in vacuo, the residue was dissolved in water, filtered and treated with excess aqueous Me₄NBr. The precipitate obtained was separated and dried in vacuo over P₂O₅. 3.27 g (69%) of light-yellow crystals was obtained, m.p. 159–161°C (CH₃OH/H₂O). Found: C, 26.94; H, 4.62; B, 18.85; Re, 36.98. C₁₁H₂₅B₉NO₃Re calcd.: C, 26.28; H, 5.01; B, 19.35; Re, 37.03%. IR spectrum: 3040 (carborane CH), 2450–2630 (BH); 2010, 1900 (CO); 1620 cm⁻¹ (C=C).

[closo-3,3,3-(CO)₃-ReC₂B₉H₁₀-1-C(Me)=CH₂] Me₄N (IV)

A mixture of 3.18 g (7.83 mmol) of BrRe(CO)₅ in 100 ml of THF and 7.83 mmol (28.5 ml of 0.275 M solution in THF) of Na₂[1-CH₂=C(Me)-1,2-C₂B₉H₁₀] was refluxed for 20 h. After treatment analogous to that described above for III, 3.19 g (79%) was obtained, m.p. 167–168°C (CH₃OH/H₂O). Found: C, 28.81; H, 4.41; B, 18.86; Re, 36.17. C₁₂H₂₇B₉NO₃Re calcd.: C, 27.89; H, 5.27; B, 18.83; Re, 36.03%. IR spectrum: 3020 (carborane CH), 2450–2620 (BH), 2010; 1995 (CO); 1625 cm⁻¹ (C=C). ¹H NMR (C₅H₅N, HMDS, δ, ppm): s, 1.92 (CH₃), s, 3.26 (NMe₄), s, 4.22 (carborane CH), s, 4.35 (=CH₂), s, 4.73 (=CH₂).

General procedure for the syntheses of complexes II, V and VI

1 mmol of tetramethylammonium salt Ia, Ib, III or IV was suspended in 30 ml of benzene; 30 ml of 40% HBF₄ or 30 ml of 35% H₂SO₄ was added and the mixture was vigorously shaken for a few min. The benzene phase was separated and the water phase was extracted with benzene (3 × 15 ml). The combined extracts were washed with water up to pH ~ 7.0 and dried over MgSO₄. After removal of the solvent, the residue was chromatographed on silica gel (2 × 25 cm column, eluant-benzene/heptane, 1/2).

closo-3,3,3-(CO)₃-3,1,2-ReC₂B₉H₁₀⁺CH₂⁺ (II). Yield 39%, m.p. 109–110°C (benzene/heptane). Found: C, 17.52; H, 2.85; B, 23.49; Re, 44.19. C₆H₁₂B₉O₃Re

calcd.: C, 17.34; H, 2.91; B, 23.41; Re, 44.80%. IR spectrum: 3090, 3030, 3010 (carborane CH, CH₂), 2400–2600 (BH), 2085, 2030, 1995 (CO), 1440 cm⁻¹ (CH).

closio-3,3,3-(CO)₃-3,1,2-ReC₂B₉H₁₀⁺CHMe (V). Yield 47%, m.p. 109–111°C (benzene/heptane). Found: C, 19.95; H, 3.28; B, 22.49; Re, 43.27. C₇H₁₄B₉O₃Re calcd.: C, 19.57; H, 3.28; B, 22.64; Re, 43.33%. IR spectrum: 3055 (carborane CH); 3010, 2980 (CH₃); 2450–2620 (BH), 2070, 2020, 2000, 1980 (CO), 1460 cm⁻¹ (CH₃).

closio-3,3,3-(CO)₃-3,1,2-ReC₂B₉H₁₀⁺CMe₂ (VI). Yield 37%, m.p. 163–166°C (benzene/heptane). Found: C, 21.73; H, 3.55; B, 21.95; Re, 41.51. C₈H₁₆B₉O₃Re calcd.: C, 21.66; H, 3.63; B, 21.93; Re, 41.96%. IR spectrum: 3068 (carborane CH); 3023, 2975, 2920 (CH₃) 2400–2600 (BH); 2065, 2021, 2000, 1978 (CO), 1395, 1376 cm⁻¹ (CH₃).

closio-3,3,3-(CO)₃-3,1,2-ReC₂B₉H₁₀⁺-1-CH₂⁺NC₅H₅ (XI)

0.22 g (2.5 mmol) of C₅H₅N was added to 0.12 g (0.29 mmol) of II in 2 ml of C₆H₆ and 3 ml of heptane. The precipitate was filtered, washed with heptane, and dried. 0.14 g (97%) of yellow-pink crystals was obtained. M.p. 140–143°C. Found: C, 27.67; H, 3.53; B, 19.34, C₁₁H₁₇B₉NO₃Re calcd.: C, 26.70; H, 3.46; B, 19.67%. IR spectrum: 3140, 3100, 3075, 3040 (carborane CH and C₅H₅N); 2640–2400 (BH); 2020, 1910 (CO), 1635 cm⁻¹ (C₅H₅N).

closio-3,3,3-(CO)₃-3,1,2-ReC₂B₉H₁₀⁺-1-CH(Me)⁺NC₅H₅ (XII)

According to the same technique described above for XI, 0.22 g (91%) of (XII), m.p. 135–138°C (heptane/acetone), was obtained from 0.2 g (0.47 mmol) of V and 0.98 g (12.4 mmol) of C₅H₅N. Found: C, 29.04; H, 3.86; B, 19.10; N, 3.32. C₁₂H₁₉B₉NO₃Re calcd.: C, 28.33; H, 3.76; B, 19.12; N, 2.75%. IR spectrum: 3140, 3100, 3080, 3050 (carborane CH, CCH, C₅H₅N); 2970, 2930 (CH₃); 2650–2450 (BH); 2110, 1900 (CO), 1630 cm⁻¹ (C₅H₅N). ¹H NMR (acetone-*d*₆, δ, ppm, HMDS): d, 1.93 (*J* 3 Hz) (CH₃); d, 1.965 (*J* 3 Hz); q 5.33 (*J* 3 Hz); q, 5.50 (*J* 3 Hz); m, 9.09–8.26 (C₅H₅N).

closio-3,3,3-(CO)₃-3,1,2-ReC₂B₉H₁₀⁺-1-CH(Me)PPh₃ (XIII)

0.12 g (0.47 mmol) of PPh₃ was added to a solution of 0.2 g (0.47 mmol) of V in 10 ml of benzene. After 3 h of stirring at 20°C, the resulting precipitate was filtered, washed with benzene, dried and recrystallized from a THF/heptane mixture. 0.27 g (90%) was obtained. Found: P, 4.52. C₂₂H₂₉B₉O₃PRe calcd.: P, 4.72%. IR spectrum: 3010, 3040, 3080, 3100 (CH carborane, CH, Ph) 2980 (CH₃), 2450–2650 (BH); 2010, 1910 cm⁻¹ (CO).

[closio-3,3,3-(CO)₃-3,1,2-ReC₂B₉H₁₀⁺-1-CH₂CN] Me₄N (XIV)

A suspension of 1 g of NaCN in 50 ml of absolute ethanol was added to 0.12 g (0.29 mmol) of II. The mixture was shaken vigorously until complex II had completely dissolved. After 0.5 h, the alcohol was evaporated in vacuo, the residue was dissolved in 10 ml of water, filtered and treated with excess aqueous solution of Me₄NBr. The precipitate obtained was filtered and dried in vacuo over P₂O₅. 0.14 g (93%) of XIV was obtained, m.p. 128–129°C (CH₃OH/H₂O). Found: C, 25.59; H, 4.73; B, 18.77; Re, 36.16. C₁₁H₂₄B₉N₂O₃Re calcd.: C, 25.61; H, 4.69; B, 18.86; Re,

36.10%. IR spectrum: 3050 (carborane CH); 2450–2630 (BH); 2260 (CN); 2015, 1990 (CO), 1490 cm^{-1} (CH_3CH_2). ^1H NMR ($\text{C}_5\text{H}_5\text{N}$, HMDS, δ , ppm): s, 2.42 (CH_2), s, 3.28 (NMe₄), s, 4.25 (carborane CH).

[closo-3,3,3-(CO)₃-3,1,2-ReC₂B₉H₁₀-1-CH(Me)CN]Me₄N (XV)

Similar to the technique described above for XIV, 0.19 g (97%) of XV was obtained from 0.15 g (0.35 mmol) of V and 0.43 g (8.77 mmol) of NaCN in 50 ml of absolute ethanol, m.p. 118–119°C ($\text{CH}_3\text{OH}/\text{H}_2\text{O}$). Found: C, 27.06; H, 4.98; B, 18.23; Re, 35.01. $\text{C}_{12}\text{H}_{26}\text{B}_9\text{N}_2\text{O}_3\text{Re}$ calcd.: C, 27.20; H, 4.95; B, 18.36; Re, 35.14%. IR spectrum: 3060 (carborane CH); 2950, 3000 (CH_3); 2400–2650 (BH); 2250 (CN); 2007, 1900 (CO); 1485 cm^{-1} (CH_3). ^1H NMR ($\text{C}_5\text{H}_5\text{N}$, HMDS, δ , ppm): d, 1.53 (CH_3) (J 6.84 Hz) (CH_3); s, 3.28 (NMe₄); d, 3.81 (J 6.84 Hz) (CH), s, 4.20 (carborane CH), s, 4.31 (carborane CH).

Reaction of VI with NaCN

Similar to the technique described above for XV, 0.22 g (100%) of IV was obtained from 0.19 g (0.43 mmol) of VI and 0.21 g (4.28 mmol) of NaCN in 50 ml of absolute ethanol, m.p. 167–168°C ($\text{CH}_3\text{OH}/\text{H}_2\text{O}$).

[closo-3,3,3-(CO)₃-3,1,2-ReC₂B₉H₁₀CH₂SCN]Me₄N (XVI)

A mixture of 0.12 g (0.25 mmol) of II in 10 ml of absolute ethanol and 0.12 g (1.25 mmol) of KSCN was shaken vigorously until complex II had completely dissolved, then left overnight at 20°C. The solution was evaporated to dryness, dissolved in 10 ml of H_2O , filtered and treated with excess aqueous solution of Me₄NBr. The precipitate obtained was filtered and dried over P_2O_5 . 0.04 g (25%) was obtained. Found: S, 6.31, $\text{C}_{11}\text{H}_{24}\text{B}_9\text{N}_2\text{O}_3\text{ReS}$ calcd.: S, 5.85%.

[closo-3,3,3-(CO)₃-3,1,2-ReC₂B₉H₁₀-1-CH(Me)-SCN]Me₄N (XVII)

Similar to the technique described above for XVI, 0.03 g (23%) of dark-pink crystals was obtained from 0.1 g (0.23 mmol) of V in 10 ml of absolute ethanol and 0.97 g (10 mmol) of KSCN. Found: Re, 33.77. $\text{C}_{12}\text{H}_{27}\text{B}_9\text{N}_2\text{O}_3\text{ReS}$ calcd.: Re, 33.08%. IR spectrum: 3040 (carborane CH); 2890–2990 (CH_3); 2400–2600 (BH), 2070–2130 (SCN); 1920, 2020 (CO).

[closo-3,3,3-(CO)₃-3,1,2-ReC₂B₉H₁₀-1-CH(Me)-OPh]Me₄N (XVIII)

0.1 g (0.86 mmol) of PhONa was added to a solution of 0.25 g (0.58 mmol) of V. It was stirred for 0.5 h at 20°C, then evaporated to dryness, dissolved in water, filtered and treated with excess of an aqueous solution of Me₄NBr. The precipitate was filtered off, dried in vacuo over P_2O_5 , and recrystallized from a $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ mixture. 0.3 g (88%) of XVIII was obtained. Found: Re, 32.09. $\text{C}_{17}\text{H}_{31}\text{B}_9\text{ReNO}_4$ calcd.: Re, 31.20%.

[closo-3,3,3-(CO)₃-3,1,2-ReC₂B₉H₁₀-1-CH(Me)₂]Me₄N (XIX)

An excess (~ 1 g) of NaBH₄ in 50 ml of CH_3CN was added to 0.2 g (0.45 mmol) of VI. The mixture was shaken vigorously until complex VI had completely dissolved. After 0.5 h the solvent was evaporated in vacuo, the residue was dissolved in 20 ml of water, filtered and precipitated with excess of an aqueous solution of Me₄NBr. 0.22 g (93%) of XIX was obtained, m.p. 143–144°C ($\text{CH}_3\text{OH}/\text{H}_2\text{O}$).

Found: C, 28.65; H, 4.50; B, 18.83. $C_{12}H_{29}B_9NO_3Re$ calcd.: C, 27.78; H, 5.63; B, 18.75%. IR spectrum: 3050 (carborane CH); 2975, 2940 (CH_3); 2450–2620 (BH); 2000, 1990 (CO) 1480 cm^{-1} (CH_3). 1H NMR (C_5H_5N , HMDS), δ , ppm): d, 0.94 (J 6.95 Hz); d, 1.44 (J 6.95 Hz); m, 2.41 (J 6.95 Hz); s, 3.26 (NMe_4); s, 3.97 (carborane CH).

[closo-3,3,3-(CO)₃-3,1,2-ReC₂B₉H₁₀-1-Et]Me₄N (XX)

Similar to the technique described above for XIX, 0.13 g (95%) of white crystals, m.p. 161–163°C, was obtained from 0.14 g (0.32 mmol) of V and 0.8 g of $NaBH_4$ in 20 ml of CH_3CN . Found: C, 26.32; H 5.25; B 19.39; Re 37.14. $C_{11}H_{27}B_9NO_3Re$ calcd.: C, 26.17; H, 5.39; B, 19.27; Re, 36.88%. IR spectrum: 3040 (carborane CH), 2880–2980 (CH_3), 2400–2600 (BH); 1900, 2020 cm^{-1} (CO).

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