

Rhenacarborane complexes with nitrosyl and alkylidene ligands. Structures of the complexes $[\text{Re}\{=\text{C}(\text{OMe})\text{C}_6\text{H}_4\text{Me-4}\}(\text{NO})(\text{CO})(\eta^5\text{-7,8-C}_2\text{B}_9\text{H}_{11})]$ and $[\text{Re}(\text{NO})(\text{CNBu}^t)\{\eta^5,\sigma\text{-7-C}=\text{N}(\text{H})\text{Bu}^t\text{-7,8-C}_2\text{B}_9\text{H}_{10}\}]$

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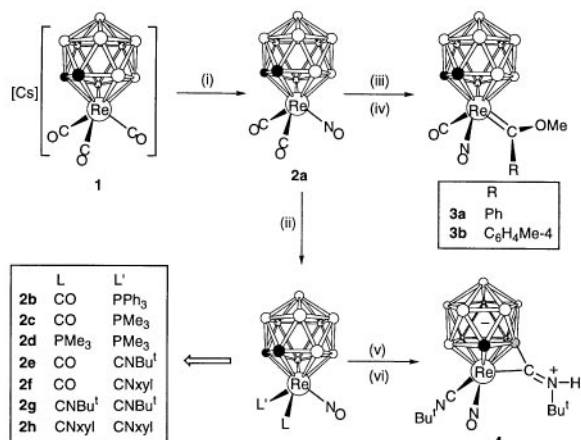
Received (in Bloomington, IN, USA) 3rd September 1999, Accepted 15th October 1999

The first examples of rhenacarborane complexes with nitrosyl ligands have been prepared and used to synthesise alkylidene(nitrosyl)rhenacarboranes and a novel complex in which a conjoined carboranyl-iminium group is bound to rhenium both through the $\eta^5\text{-C}_2\text{B}_3$ face of the cage and the iminium carbon atom.

Because of their high compatibility with other groups when ligating metal centres the cyclopentadienide anion and its derivatives rank among the most important ligands in organo-transition metal chemistry.¹ Formally isolobal with $[\text{C}_5\text{H}_5]^-$ the dicarbollide dianion [*nido*-7,8- $\text{C}_2\text{B}_9\text{H}_{11}$]²⁻ and its C-substituted derivatives have been known to form metal complexes for over 30 years.² However, the chemistry of these species is much less extensive than that of their cyclopentadienide analogs.³ Herein we report the first rhenacarborane carbonyl nitrosyl compound, a useful synthon for preparing other species including the first isolable complexes with alkylidene groups ligating a metal centre in an $\text{M}(\eta^5\text{-7,8-R}_2\text{-7,8-C}_2\text{B}_9\text{H}_9)$ (R = H, alkyl, aryl) group (Scheme 1).

Treatment of $\text{Cs}[\text{Re}(\text{CO})_3(\eta^5\text{-7,8-C}_2\text{B}_9\text{H}_{11})]$ **1a** in tetrahydrofuran (THF) with $[\text{NO}][\text{BF}_4]$ gave the stable complex $[\text{Re}(\text{NO})(\text{CO})_2(\eta^5\text{-7,8-C}_2\text{B}_9\text{H}_{11})]$ **2a** in high yield.[†] A range of complexes **2b–2h** have been synthesized from **2a** by substitution of one or both CO ligands. In a typical reaction **2a** reacts with excess CNBu^t in THF to give yellow crystals of $[\text{Re}(\text{NO})(\text{CNBu}^t)_2(\eta^5\text{-7,8-C}_2\text{B}_9\text{H}_{11})]$ **2g**.[†]

Compound **2a** was treated initially with LiPh or $\text{Li}[\text{C}_6\text{H}_4\text{Me-4}]$ and then with $[\text{Me}_3\text{O}][\text{BF}_4]$. Column chromatography on silica gel of the resulting mixture gave the alkylidene complexes $[\text{Re}\{=\text{C}(\text{OMe})\text{R}\}(\text{NO})(\text{CO})(\eta^5\text{-7,8-C}_2\text{B}_9\text{H}_{11})]$ (R = Ph **3a**, $\text{C}_6\text{H}_4\text{Me-4}$ **3b**), respectively. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum[†] of **3b** displays a diagnostic resonance for the alkylidene carbon nucleus at δ 295.1 to be compared with the NMR signal for this



Scheme 1 Reagents and conditions: i, $[\text{NO}][\text{BF}_4]$, THF, -80°C ; ii, $\text{L/L}'$, THF, reflux; iii, LiR , Et_2O , -80°C ; iv, $[\text{Me}_3\text{O}][\text{BF}_4]$, -50°C ; v, $\text{L} = \text{L}' = \text{CNBu}^t$; LiPh , Et_2O , -50°C ; vi, HBF_4OEt_2 , -80°C . Key: $\circ = \text{BH}$, $\bullet = \text{CH}$, $\odot = \text{C}$, $\text{xy}^l = \text{C}_6\text{H}_3\text{Me}_2\text{-2,6}$.

nucleus at δ 289.2 in the isolobal cation $[\text{Re}\{=\text{C}(\text{OMe})\text{C}_6\text{H}_4\text{Me-4}\}(\text{NO})(\text{CO})(\eta\text{-C}_5\text{H}_5)]^+$.⁵ The appearance in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **3b** of only one signal for the OMe group indicated that only one enantiomeric pair of molecules was formed. An X-ray crystal structure analysis[‡] established the structure (Fig. 1) and showed that the OMe and NO groups are transoid to one another [$\phi(\text{NReC}(9)\text{O}(4))$ 163.5°]. The $\text{Re}-\text{C}(9)$ bond distance [$2.052(9)$ Å] is similar to that found [$1.949(6)$ Å] for the alkylidene ligand in $[\text{Re}\{=\text{CHPh}\}(\text{NO})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)][\text{PF}_6]$.⁶ We have previously observed that when alkylidene ligands are exopolyhedral substituents on a tungsten centre in a *closo*-3,1,2- WC_2B_9 tungstacarborane complex they undergo rapid and irreversible hydroboration by an adjacent B–H bond in the cage $\overline{\text{CCBBB}}$ coordinating face.⁷ Thus the formation and isolation of the complexes **3** was perhaps unexpected in icosahedral metallocarborane chemistry. Grimes and coworkers⁸ have recently isolated the first transition metal alkylidene complex incorporating a sub-icosahedral metallocarborane, viz. $[\text{RuCo}\{=\text{C}(\text{OMe})\text{Ph}\}(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)(\eta^5\text{-2,3-Et}_2\text{-5-Cl-2,3-C}_2\text{B}_3\text{H}_2)]$. This molecule comprises a ruthenium dicarbonyl phenylmethoxyalkylidene fragment pentacoordinated by the C_2B_3 face of a *nido*-cobaltacarborane ligand.

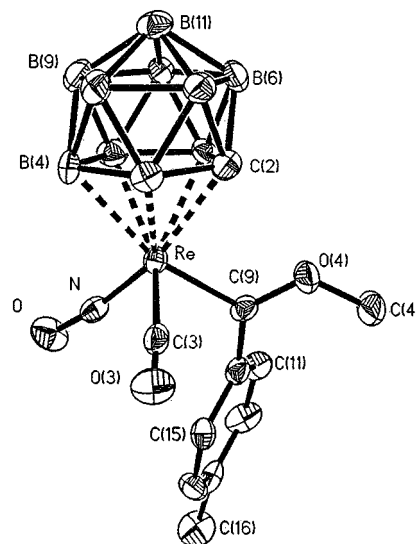
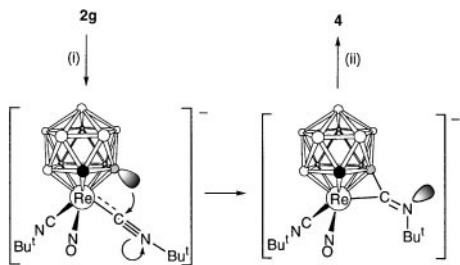


Fig. 1 Molecular structure of **3b** (thermal ellipsoids with 40% probability). Selected distances (Å) and angles ($^\circ$): $\text{Re}-\text{N}$ 1.768(8), $\text{Re}-\text{C}(3)$ 1.963(10), $\text{Re}-\text{C}(9)$ 2.052(9), $\text{N}-\text{O}$ 1.188(9), $\text{C}(3)-\text{O}(3)$ 1.130(11), $\text{C}(9)-\text{O}(4)$ 1.321(11); $\text{N}-\text{Re}-\text{C}(3)$ 92.7(3), $\text{N}-\text{Re}-\text{C}(9)$ 93.4(4), $\text{C}(3)-\text{Re}-\text{C}(9)$ 88.7(4), $\text{O}-\text{N}-\text{Re}$ 172.0(7), $\text{O}(3)-\text{C}(3)-\text{Re}$ 175.4(9), $\text{O}(4)-\text{C}(9)-\text{Re}$ 117.2(6), $\text{C}(9)-\text{O}(4)-\text{C}(4)$ 124.3(8), $\text{C}(10)-\text{C}(9)-\text{Re}$ 124.4(7).

Reaction of LiPh with the bis(isonitrile)nitrosyl compound **2g** followed by addition of $\text{HBF}_4\text{Et}_2\text{O}$ affords the novel complex $[\text{Re}(\text{NO})(\text{CNBu}^t)\{\eta^5,\sigma\text{-7-C}=\text{N}(\text{H})\text{Bu}^t\text{-7,8-C}_2\text{B}_9\text{H}_{10}\}]$ **4**. Evidently the lithium reagent deprotonates one of the CH groups of the carborane cage to give an intermediate which on



Scheme 2 Reagents and conditions: i, LiPh, Et₂O, -50 °C; ii, HBF₄·OEt₂, -80 °C. Key: ○ = BH, ● = CH, ⊙ = C.

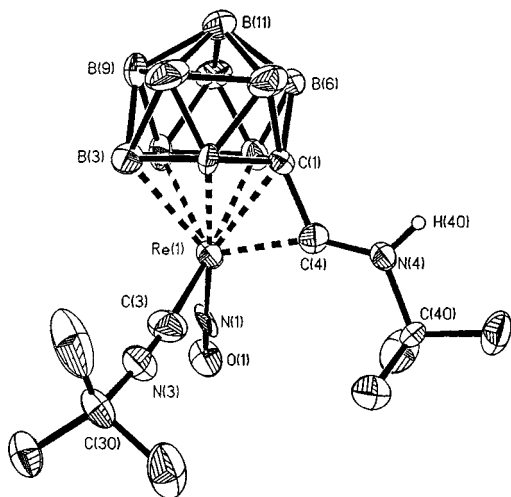


Fig. 2 Molecular structure of one of the independent molecules found in the asymmetric unit of **4** (thermal ellipsoids with 40% probability). Selected distances (Å) and angles (°): Re(1)–N(1) 1.769(11), Re(1)–C(4) 2.000(13), Re(1)–C(3) 2.02(2), C(1)–C(4) 1.49(2), N(1)–O(1) 1.206(12), C(3)–N(3) 1.14(2), C(4)–N(4) 1.29(2); N(1)–Re(1)–C(4) 111.9(5), N(1)–Re(1)–C(3) 93.0(5), C(4)–Re(1)–C(3) 101.3(5), O(1)–N(1)–Re(1) 174.1(11), N(3)–C(3)–Re(1) 173.3(14), C(3)–N(3)–C(30) 175(2), N(4)–C(4)–C(1) 127.6(12), N(4)–C(4)–Re(1) 154.7(11), C(1)–C(4)–Re(1) 76.2(7), C(4)–N(4)–C(40) 124.3(11).

protonation yields **4** (Scheme 2), formulated as a charge-compensated species. The structure was established by X-ray diffraction[‡] (Fig. 2). Atom C(4) bridges the Re–C(1) connectivity [C(1)–C(4) 1.49(2), Re(1)–C(4) 2.000(13) Å]. Although the C(4)–N(4) distance [1.29(2) Å] is longer than C(3)–N(3) [1.14(2) Å] in the ligated isonitrile molecule it is somewhat shorter than that expected (1.34 Å) for a C=N double bond.⁹ The NH proton is recognisable in the ¹H NMR spectrum[†] as a broad signal at δ 8.93, while in the ¹³C{¹H} NMR spectrum the iminium carbon atom, which is both bound to the cage carbon vertex and to the rhenium centre (δ 218.8), can be readily distinguished from the ligating carbon atom of the classical isonitrile ligand (δ 137.7). The formation of **4** appears to be regioselective, since only one of several possible diastereomeric pairs of enantiomers was isolated. This may in part be due to the directive influence of the NO ligand and further studies with these complexes are in progress to examine this effect.

We thank the Robert A. Welch Foundation for support (Grant AA-1201).

Notes and references

[†] **2a**: Bright yellow microcrystals; yield 89%. Anal. Calc. for C₄H₁₁B₉NO₃Re: C, 11.9; H, 2.7; N, 3.5. Found: C, 12.4; H, 3.0; N, 3.3%;

IR (CH₂Cl₂): ν_{max}(CO) 2093, 2034 cm⁻¹, ν_{max}(NO) 1776 cm⁻¹; ¹H NMR (360.13 MHz, CD₂Cl₂) δ 3.64 (s br, 2H, CH); ¹³C{¹H} NMR (90.56 MHz, CD₂Cl₂) δ 187.4 (s, CO), 43.8 (s br, CH); ¹¹B{¹H} NMR (115.55 MHz, CD₂Cl₂) δ 1.7 (s, 1 B), -3.9 (s, 3 B), -11.4 (s, 2 B), -16.6 (s, 3 B).

2g: Yellow microcrystals; yield 67%. Anal. Calc. for C₁₂H₂₉B₉N₃ORe: C, 28.0; H, 5.7; N, 8.2. Found: C, 28.2; H, 5.8; N, 8.1%; IR (CH₂Cl₂): ν_{max}(NC) 2174, 2137 cm⁻¹, ν_{max}(NO) 1721 cm⁻¹; ¹H NMR (360.13 MHz, CD₂Cl₂) δ 3.11 (s br, 2H, CH), 1.58 (s, 18H, CMe₃); ¹³C{¹H} NMR (90.56 MHz, CD₂Cl₂) δ 135.8 (s br, CN), 59.9 (s, CMe₃), 39.9 (s br, CH), 31.1 (s, CMe₃). ¹¹B{¹H} NMR (115.55 MHz, CD₂Cl₂) δ -4.2 (s, 1 B), -4.8 (s, 1 B), -7.3 (s, 2 B), -11.4 (s, 2 B), -19.6 (s, 3 B).

3b: Yellow microcrystals; yield 20% (unoptimised). Anal. Calc. for C₁₂H₂₁B₉NO₃Re: C, 28.2; H, 4.1; N, 2.7. Found: C, 28.4; H, 4.0; N, 2.7%; IR (CH₂Cl₂): ν_{max}(CO) 2029 cm⁻¹, ν_{max}(NO) 1750 cm⁻¹; ¹H NMR (360.13 MHz, CD₂Cl₂) δ 7.34, 7.39 [AB, 4H, C₆H₄, J(AB) 8 Hz], 4.53 (s, 3H, OMe), 3.05, 3.32 (s × 2, 2H, CH), 2.43 (s, 3H, Me-4); ¹³C{¹H} NMR (90.56 MHz, CD₂Cl₂) δ 295.1 (s, =C), 195.9 (s, CO), 147.6, 145.4, 130.0, 127.0 (s × 4, C₆H₄), 69.7 (s, OMe), 45.3, 44.4 (s br × 2, CH), 21.8 (s, Me-4); ¹¹B{¹H} NMR (115.55 MHz, CD₂Cl₂) δ -2.4 (s, 1 B), -3.2 (s, 1 B), -5.4 (s, 2 B), -11.8 (s vbr, 2 B), -17.1 (s vbr, 2 B), -18.4 (s, 1 B).

4: Yellow microcrystals; yield 50%. Anal. Calc. for C₁₂H₂₉B₉N₃ORe: C, 28.0; H, 5.7; N, 8.2. Found: C, 28.0; H, 5.7; N, 8.2%; IR (CH₂Cl₂): ν_{max}(NC) 2147, 1587 cm⁻¹, ν_{max}(NO) 1667 cm⁻¹; ¹H NMR (360.13 MHz, CD₂Cl₂) δ 8.93 (s br, 1H, NH), 1.59 (s br, 1H, CH), 1.50, 1.51 (s × 2, 18 H, CMe₃); ¹³C{¹H} NMR (90.56 MHz, CD₂Cl₂) δ 218.8 (s, CC=N), 137.7 (s br, CNBu^t), 59.7, 58.2 (s × 2, CMe₃), 57.7 (s br, CC=N), 35.7 (s br, CH), 31.1, 28.8 (s × 2, CMe₃); ¹¹B{¹H} NMR (115.55 MHz, CD₂Cl₂) δ 0.5 (s, 1 B), -1.4 (s, 1 B), -9.2 (s, 1 B), -12.4 (s, 2 B), -14.8 (s, 1 B), -17.2 (s, 1 B), -21.8 (s, 1 B), -29.4 (s, 1 B).

[‡] *Crystal data*: Enraf-Nonius CAD4 diffractometer, Mo-Kα radiation (λ = 0.71073 Å), graphite-monochromated, Lorenz polarization and empirical absorption corrections. The structures were solved by direct methods and refined with the full-matrix, least-squares method on F² (SHELXL). **3b**: Crystals from CH₂Cl₂-toluene at -20 °C, C₁₂H₂₁B₉NO₃Re, 510.79, triclinic, space group P1̄ (no. 2), a = 6.977(3), b = 10.9320(11), c = 12.6768(8) Å, α = 96.151(7), β = 99.368(14), γ = 95.04(2)°, Z = 2, U = 943.1(4) Å³, μ(Mo-Kα) = 6.5 mm⁻¹, T = 293(2) K, ω scan mode, 3583 reflections measured, 3288 were unique (R_{int} = 0.0321) and 2769 observed [I > 2σ(I)], R₁ = 0.0429, wR₂ = 0.0919 [for 2769 reflections with I > 2σ(I)], R₁ = 0.0573, wR₂ = 0.0981 (for all 3288 data). **4**: crystals from CH₂Cl₂-light petroleum, C₁₂H₂₉B₉N₃ORe, 514.87, monoclinic, space group P2₁/n (no. 14), a = 18.636(3), b = 11.757(2), c = 21.299(6) Å, β = 109.11(2)°, Z = 8, U = 4410(2) Å³, μ(Mo-Kα) = 5.5 mm⁻¹, T = 293(2) K, ω-2θ scan mode, 5667 reflections measured, 5302 were unique (R_{int} = 0.0516) and 3797 observed [I > 2σ(I)], R₁ = 0.0512, wR₂ = 0.0889 [for 3797 reflections with I > 2σ(I)], R₁ = 0.0863, wR₂ = 0.0991 (for all 5302 data). CCDC 182/1453. See <http://www.rsc.org/suppdata/cc/1999/2385/> for crystallographic files in .cif format.

- C. Janiak and H. Schumann, *Adv. Organomet. Chem.*, 1991, **33**, 291.
- M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren and P. A. Wegner, *J. Am. Chem. Soc.*, 1968, **90**, 879.
- R. N. Grimes, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon Press, Oxford, 1995; vol. 1 (ed. C. E. Housecroft), ch. 9, p. 399.
- M. F. Hawthorne and T. D. Andrews, *J. Am. Chem. Soc.*, 1965, **87**, 2496; A. Zalkin, T. E. Hopkins and D. H. Templeton, *Inorg. Chem.*, 1966, **5**, 1189.
- J. B. Sheridan, J. R. Johnson, B. M. Handwerker and G. L. Geoffroy, *Organometallics*, 1988, **7**, 2404.
- W. A. Kiel, G.-Y. Lin, A. G. Constable, F. B. McCormick, C. E. Strouse, O. Eisenstein and J. A. Gladysz, *J. Am. Chem. Soc.*, 1982, **104**, 4865.
- S. A. Brew and F. G. A. Stone, *Adv. Organomet. Chem.*, 1993, **35**, 135.
- K. E. Stockman, M. Sabat, M. G. Finn and R. N. Grimes, *J. Am. Chem. Soc.*, 1992, **114**, 8733.
- F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.

Communication 9/07144J