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Formation of a caged rhodium complex *via* an intramolecular, metal-mediated [2 + 2 + 1] cycloaddition of alkynes and CO †

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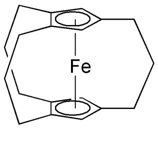
An organometallic rhodium cage complex has been synthesized by a metal-mediated intramolecular [2 + 2 + 1] cycloaddition, in the first example of such a process where the cyclisation step completes a cage around the metal centre.



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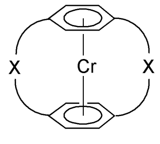
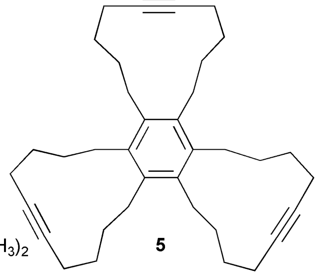


2 X = CH_2CH_2
3 X = $CH_2CH_2CH_2$
4 X = $Si(CH_3)_2Si(CH_3)_2$



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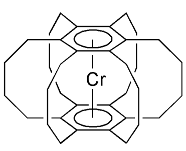

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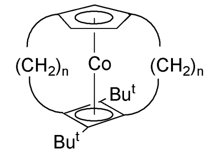
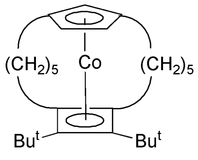


7 n = 3, 4, or 5



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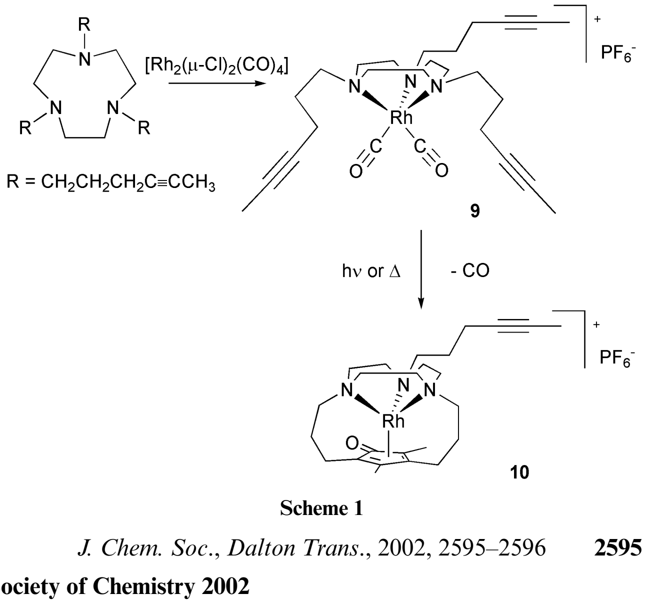
Fascinating opportunities exist at the intersection of organometallic chemistry and cyclophane chemistry. As early as 1960, Cram and Wilkinson[1] suggested the possibility of encapsulating a metal within a cyclophane. Ferrocenophanes such as **1** have been known for almost 40 years,[2] but their syntheses are tedious and lengthy and overall yields are low. The cyclophane complexes **2** and **3** have been synthesized from the corresponding paracyclophanes *via* metal atom vapour techniques,[3,4] while a combination of a metal atom vapour reaction and a subsequent dechlorination step was used to synthesize **4**.[5] Although these syntheses were short and afforded products in quantities of up to 60 mg,[5] the yields of **2**–**4** were again very low (<4%). The difficult and low-yielding nature of these syntheses may be the reason why there has been limited study of the chemistry of organometallic cage complexes, whereas more readily accessible caged coordination complexes such as azacryptands[6] have received intense scrutiny. Gladysz and co-workers proposed a novel approach to a caged chromium complex. They suggested[7] that co-condensation of 1,7-cyclododecadiyne with chromium atoms would initially yield (*via* metal-mediated alkyne cyclotrimerisation) the trimer **5** with a Cr atom bound to the arene ring, and that subsequent intramolecular cyclotrimerisation of the pendant alkynes would lead to **6**. They failed to obtain any of the desired cage complex, instead isolating only **5** and polymeric by-products. Recently, however, Gleiter and coworkers[8] synthesized the cobalt cyclophanes **7** and **8** *via* intramolecular [2 + 2] cycloaddition reactions of precursors bearing pendant alkyne groups. We have also been investigating the reactivity of metal complexes bearing pendant alkyne groups,[9,10] and here report a new intramolecular [2 + 2 + 1] cycloaddition[11] that leads to a novel caged rhodium complex.

The pendant alkyne complex **9** was synthesized by reaction of the corresponding triazacyclononane with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ in acetone (Scheme 1).[9] Although **9** is stable in the solid state, in solution it undergoes loss of one equivalent of CO and an intramolecular [2 + 2 + 1] cycloaddition of two pendant alkynes and the remaining CO, to form the cage complex **10**.‡ Conversion of **9** to **10** was most effectively achieved by heating acetone solutions containing **9** at 50 °C for 8 h, but could also be achieved by irradiation of the solutions (tungsten or mercury lamps, Pyrex vessel). NMR studies indicate that, although **10** was the only well-defined product (*ca.* 50% yield), other products were also formed, their broad spectral features suggesting that they may be oligomeric materials arising from intermolecular coupling reactions. We have not detected any intermediates in the conversion of **9** to **10**, nor have we seen any evidence for diastereomers of **10** (*i.e.*, alternative substitution patterns about the cyclopentadienone ring). Complex **10** was conveniently isolated from reaction mixtures by crystallization as its hexafluorophosphate salt. Due largely to mechanical losses, the isolated yield of **10** was lower (16%) than that established by NMR spectroscopy.

The structure of **10**·PF_6 was determined by a low-temperature single crystal X-ray study (Fig. 1). One formula unit, solvated with a lattice molecule of nitromethane and devoid of crystallographic symmetry, comprises the asymmetric unit of the structure. The cyclopentadienone unit is bound quasi-η^4 through the alkenyl carbons, as indicated by the non-planar nature of the five-membered ring, with the carbonyl carbon being significantly further from the rhodium centre than are the four alkenyl carbons. The asymmetry in the equatorial substituents at N(1,4,7) (one pendant, the other two cyclic) is not reflected in the conformation of the triaza-ring, which



Scheme 1

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† Electronic supplementary information (ESI) available: spectroscopic data for **10**. See http://www.rsc.org/suppdata/dt/b2/b202713e/

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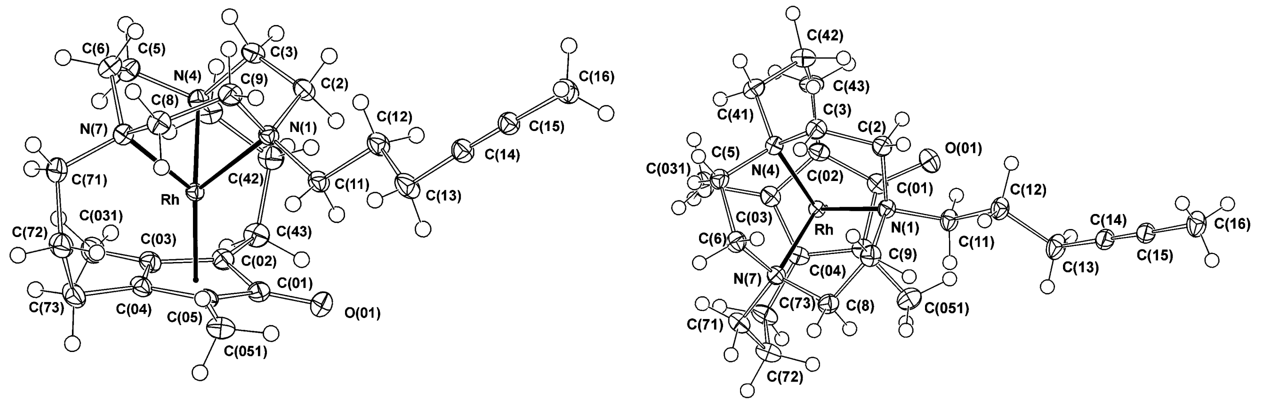

Fig. 1 Projections of the cation **10**, showing 50% displacement amplitude ellipsoids for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. Rh–N(1,4,7) 2.219(2), 2.128(1), 2.175(1); Rh–C(01–5) 2.364(1), 2.134(2), 2.102(2), 2.126(2), 2.183(1); C(01)–O(01), C(02,5) 1.255(2), 1.470(2), 1.479(3); C(03)–C(02,4) 1.450(3), 1.441(3); C(04)–C(05) 1.425(3); C(14)–C(15) 1.199(3) Å. C,O(01) lie 0.203(3), 0.366(4) Å out of the C(02–5) plane ($\chi^2 = 0.6$). Torsion angles in the bonds around the triaza-ring are, successively from N(1)–C(2), −69.2(2), −45.4(2), 131.0(2), −67.8(2), −48.8(2), 134.3(2), −66.6(2), −48.9(2), 134.7(2)°.

maintains its familiar quasi-C_3 symmetry, although some strain is evident in the values for the angles at C(41, 42, 71, 72) [114.4(1), 114.9(2), 116.1(2), 115.0(2)°].

The ^{1}H and ^{13}C NMR spectra of solutions containing the cation **10** were complex, but partial assignments were possible, using a combination of 1D and 2D NMR techniques (HMBC, for two- and three-bond ^{1}H–^{13}C correlation; HSQC, for one-bond ^{1}H–^{13}C correlation). The ^{13}C NMR signals for the cyclopentadienone carbons are of interest: consistent with the cyclopentadienone ligand being bound in η^4-fashion, the four alkenyl carbons show rhodium–carbon coupling but the carbonyl carbon does not. Interestingly, of the signals due to the alkenyl carbons, only the signal for C(04) is sharp, with the other three signals being somewhat broadened, the reason for which is unknown. The ^{1}H NMR spectrum shows three distinct methyl resonances, the one due to the remaining pendant alkyne being a triplet because of long-range ^{1}H–^{1}H coupling across the triple bond, while those associated with the cyclopentadienone unit appear as singlets.

Complex **10** is air-stable in the solid state and in solution, and exposure of a CD_3NO_2 solution of **10** to air for over three months caused no change in the ^{1}H NMR spectrum. Preliminary studies into the electrochemistry of **10** indicate that the complex undergoes a quasi-reversible single electron oxidation (Fig. 2). Interestingly, under similar conditions the related COD complex **11**[9] only undergoes an irreversible oxidation process (Fig. 2), similar to that reported for [(Me$_3$TACN)-Rh(COD)]PF$_6$.[12]

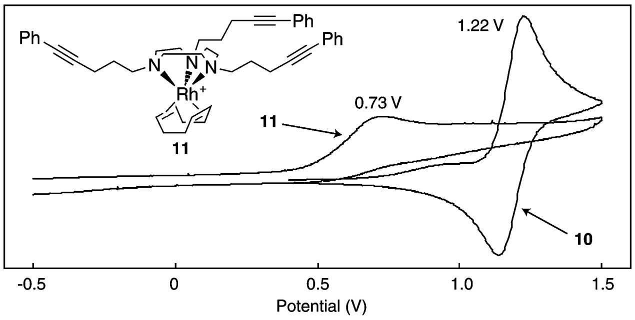

Fig. 2 Cyclic voltammograms for **10**·PF$_6$ and **11**·PF$_6$ [0.1 M Bu$_4$NPF$_6$ in acetonitrile under Ar, Pt working electrode, Ag/AgCl reference (E_P ferrocene = 0.47 V), scan rate 200 mV s^{-1}].

The straightforward cycloaddition route that leads to **10** should be applicable to the synthesis of other transition metal cage complexes derived from alkynyltriazacyclononanes, alkynyltriphosphacyclododecanes and related ligand systems, and should facilitate further studies of this fascinating class of compounds.

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Notes and references

‡ **10**: A deoxygenated solution of **9**[9] (8.6 mg, 13 mmol) in acetone (1 mL) in a sealed tube with an evacuated headspace (1.5 mL) was heated for *ca.* 10 h at 40–50 °C. The solution was concentrated to dryness and the residue was recrystallised by the vapour diffusion of solvents between neat benzene and a solution of the residue in wet nitromethane (not deoxygenated), to give **10** as yellow–orange crystals (1.5 mg, 16%) (Found C, 44.29; H, 5.94; N, 6.11. $C_{25}H_{39}F_6N_3OPRh\cdot H_2O$ requires C, 44.06; H, 6.36; N, 6.17%). Crystals suitable for X-ray studies were grown by the vapour diffusion of solvents between neat benzene and a solution of **10** in dry CH_3NO_2.

10·PF$_6$·CH$_3$NO$_2$ ≡ $C_{26}H_{42}F_6N_4O_3PRh$, M = 706.5, triclinic, $P\bar{1}$, a = 10.379(1), b = 10.692(1), c = 15.714(2) Å, α = 104.826(2), β = 92.569(2), γ = 118.094(2)°, V = 1459 Å^3, D_c (Z = 2) = 1.60$_8$ g cm^{-3}. 29011 reflections (full sphere) [multiscan absorption-corrected area detector CCD diffractometer data (Bruker AXS instrument, monochromatic Mo-Kα radiation, (λ = 0.7107$_3$ Å), ω-scans ($2\theta_{max}$ = 75°)], T *ca.* 153 K, μ_{Mo} = 7.1 cm^{-1}, '$T_{min,max}$ = 0.69, 0.84) merged to 14718 unique (R_{int} = 0.027), 12801 with $F > 4\sigma(F)$ refining to conventional R = 0.033, R_w [weights: $\{\sigma^2(F) + 0.0004F^2\}^{-1}$] = 0.045 [non-hydrogen atom thermal parameter forms anisotropic, $(x, y, z, U_{iso})_H$ refined]. CCDC reference number 160382. See http://www.rsc.org/suppdata/dt/b2/b202713e/ for crystallographic data in CIF or other electronic format.

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