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## Calcium, Strontium, and Barium Cyclo-octatetraenediyl Complexes: Synthesis of a Stable Phosphacyclopropane (Structurally Authenticated)

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Cocondensation of calcium, strontium, or barium vapours with excess cot (cyclo-octatetraene) and thf (tetrahydrofuran) affords sparingly thf-soluble, pyrophoric  $M(\text{cot})(\text{thf})_n$  (**1**), which decomposes at *ca.* 60 °C *in vacuo* to  $M(\text{cot})$  (**2**),  $M = \text{Ca}, \text{Sr}, \text{or Ba}$ ; reactions of (**2**) with some organic halides are reported along with formation of a pyridine adduct,  $M(\text{cot})(\text{pyridine})_n$  (**3**), and from (**2**) and  $\text{RPh}_2\text{C}(\text{C}_5\text{H}_4\text{N}-2)$  the synthesis of a thermally stable phosphacyclopropane,  $\text{RP}(\text{C}_8\text{H}_8)$  [ $\text{R} = \text{Ph}_2\text{C}(\text{C}_5\text{H}_4\text{N}-2)$ ].

Within the realm of Group 2 chemistry, cyclo-octatetraenediyl ( $\text{cot}^{2-}$ ) complexes are documented for magnesium<sup>1,2</sup> but not for calcium, strontium, and barium. Overall, the organometallic chemistry of these elements is considerably less developed than that of magnesium,<sup>3</sup> although several recent reports, mainly on cyclopentadienyl compounds,<sup>4</sup> indicate growing interest in the area. Here we report the synthesis of  $\text{cot}^{2-}$  complexes of calcium, strontium, and barium, and the reactions of the derived solvent-free compounds,  $M(\text{cot})$ , with pyridine, with a variety of organic halides, and with a new highly hindered alkyl dichlorophosphorus(III) compound to form a stable phosphacyclopropane (9-phosphabicyclo-[6.1.0]nona-2,4,6-triene) which has been structurally characterized.

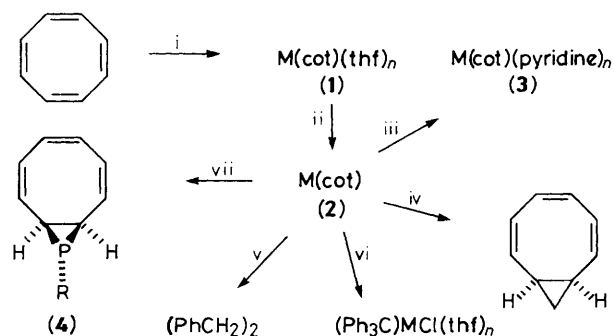
Cocondensation of metal with cyclo-octatetraene (cot) and thf (tetrahydrofuran) at -196 °C yields a black matrix which on warming to room temperature affords cream, sparingly soluble  $M(\text{cot})(\text{thf})_n$  (**1**). These complexes on heating *in vacuo* at *ca.* 60 °C, yield  $M(\text{cot})$  (**2**) as white powders (m.p. >300 °C, yield *ca.* 80% based on metal consumed); the analogous magnesium compound  $\text{Mg}(\text{cot})$  is similarly formed from  $\text{Mg}(\text{cot})(\text{thf})_{2.5}$ .<sup>1</sup> Addition of pyridine to (**2**) yields  $M(\text{cot})(\text{pyridine})_n$  (**3**), as sparingly soluble orange powders which, like (**1**) and (**2**), are pyrophoric.

Compounds (**1**)—(**3**)† most likely have polyhapto ligand-to-metal interactions, albeit with a high ionic character, and/or a polymeric structure because of their low solubility in organic solvents which precluded solution n.m.r. spectroscopic studies. A compound related to the present study is  $[\text{Yb}(\eta-$

$\text{cot})(\text{pyridine})_3]$  [derived from  $\text{Yb}(\text{cot})^5$  and pyridine] which has a symmetrically bound dianion; analogous structures are likely for (**3**), and also (**1**).

Details of the reactions of (**2**) with various organic halides are shown in Scheme 1. Dichloromethane yields bicyclo-[6.1.0]nonatriene as the major product (*ca.* 50%), which has previously been prepared in a similar manner using  $\text{Li}_2(\text{cot})$  or  $\text{K}_2(\text{cot})$ .<sup>6</sup> Benzyl chloride yields the Wurtz coupled product, as for  $\text{Mg}(\text{cot})(\text{thf})_{2.5}$ ,<sup>7</sup> and trityl chloride in contrast affords the corresponding metal organic halide. Thus, (**2**) can act as a source of metal like magnesium anthracene complexes reacting with benzylic halides,<sup>8</sup> or as an organic nucleophile.

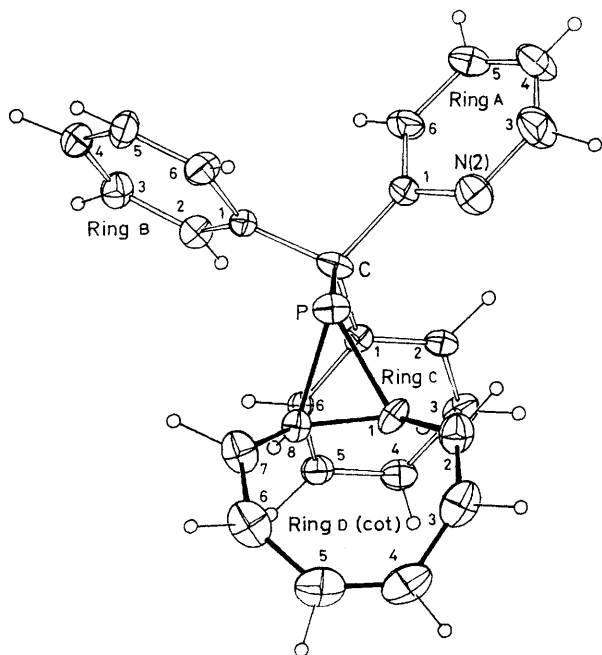
The thf-free complexes (**2**) have also been characterized by formation of phosphine derivatives; treatment with  $\text{RPh}_2\text{C}(\text{C}_5\text{H}_4\text{N}-2)$



**Scheme 1.** Reagents and conditions: i, metal vapour, thf, -196 °C; ii, *ca.* 60 °C, *in vacuo*; iii, pyridine, *ca.* 20 °C; iv,  $\text{CH}_2\text{Cl}_2$ , thf, 0 °C; v,  $\text{PhCH}_2\text{Cl}$ , thf, 0 °C; vi,  $\text{Ph}_3\text{C}(\text{C}_5\text{H}_4\text{N}-2)$ , thf, -78 °C.

$M = \text{Ca}, \text{Sr}, \text{Ba}$ ;  $\text{R} = \text{Ph}_2\text{C}(\text{C}_5\text{H}_4\text{N}-2)$

† Characterization of (**1**)—(**3**): microanalyses on (**1**) and (**3**) were variable and attempts to determine Lewis base/ligand ratios by treatment with acids and  $\text{CCl}_4$  were plagued by spontaneous ignitions; i.r. spectra showed thf metal-bound in (**1**), pyridine metal-bound and the absence of thf in (**3**), and (**2**) devoid of thf; microanalyses of (**2**) were satisfactory for hydrogen but typically 3% low in carbon.



**Figure 1.** Molecular projection of compound (4), showing 20% thermal ellipsoids for the non-hydrogen atoms, and arbitrary radii for hydrogen atoms. Selected bond distances (Å) and angles (°) are P–C, 1.951(6); P–C(d1,8), 1.842(5), 1.813(5); endocyclic distances C(d1)–C(d2), 1.477(9); C(d2)–C(d3), 1.332(9); C(d3)–C(d4), 1.441(11); C(d4)–C(d5), 1.301(12); C(d5)–C(d6), 1.430(11); C(d6)–C(d7), 1.360(9); C(d7)–C(d8), 1.495(9); C(d1)–C(d8), 1.460(9); C–P–C(d1,8), 105.8(3), 108.9(3); C(d1)–P–C(d8), 47.1(3); P–C(d1)–C(d2), 118.2(4); P–C(d8)–C(d7), 114.5(4); endocyclic angles C(d1)–C(d8) in sequence round the ring 127.9(5), 128.8(7), 131.4(8), 125.7(7), 135.4(7), 129.2(7), 128.1(6), 126.3(6).

R =  $\text{Ph}_2\text{C}(\text{C}_5\text{H}_4\text{N}-2)$ , yields the phosphacyclopropane, (4).<sup>‡</sup> Here these complexes act as a source of  $\text{cot}^{2-}$ , as does the related magnesium complex  $\text{Mg}(\text{cot})(\text{thf})_2$ ,<sup>5</sup> with  $\text{RPhCl}_2$ , also affording (4) in similar yield, ca. 37%. Compound (4) has high thermal stability with respect to rearrangement to a 9-substituted-9-phosphabicyclo[4.2.1]nonatriene (phosphorus spanning C-1 and C-4 centres of  $\text{cot}^{2-}$ ), being unaffected at 100 °C for several hours in toluene. Unless the alkyl group on phosphorus is highly hindered,<sup>9</sup> phosphacyclopropane derivatives of  $\text{cot}$  readily undergo such rearrangement.<sup>10</sup> An X-ray

structure determination of (4)<sup>§</sup> establishes an *anti* stereochemistry (Figure 1) as predicted on the basis of the large steric hindrance of R. The N-functionality appears to be passive towards the P-centre; P–cot distances, mean 1.82<sub>8</sub> Å, are significantly shorter than in the related 'less strained' ring system of 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene, 1.85<sub>0</sub> Å,<sup>10</sup> and in the phosphacyclopropane  $\text{PhP}(\text{CPh}_2\text{C}(\text{SiMe}_3)_2)_2$ , 1.88 Å,<sup>11</sup> which has a larger propane ring C–C distance, 1.56 Å, than in (4), 1.495(9) Å.

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## References

- H. Lehmkuhl, S. Kintopf, and K. Mehler, *J. Organomet. Chem.*, 1972, **46**, C1; T. Alonso, S. Harvey, P. C. Junk, C. L. Raston, B. W. Skelton, and A. H. White, *Organometallics*, 1987, **6**, 2110.
- W. J. Richter, *Chem. Ber.*, 1985, **118**, 97.
- C. L. Raston and G. Salem, in 'Chemistry of the Metal Carbon Bond,' vol. 4, ed. F. R. Hartley, Wiley, Chichester, 1987, ch. 2.
- L. M. Engelhardt, P. C. Junk, C. L. Raston, and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1988, 1500; R. A. Andersen, R. Blom, J. M. Boncella, C. J. Burns, A. Haaland, and H. V. Volden, *J. Organomet. Chem.*, 1986, **312**, C49; R. A. Andersen, R. Blom, J. M. Boncella, C. J. Burns, and H. V. Volden, *Acta Chem. Scand., Ser. A*, 1987, **41**, 24; R. A. Andersen, R. Blom, C. J. Burns, and H. V. Volden, *J. Chem. Soc., Chem. Commun.*, 1987, 768; C. J. Burns and R. A. Andersen, *J. Organomet. Chem.*, 1987, **325**, 31; M. J. McCormick, R. A. Williams, L. J. Levine, and T. P. Hanusa, *Polyhedron*, 1988, **7**, 725; R. A. Williams, T. P. Hanusa, and J. C. Huffman, *J. Chem. Soc., Chem. Commun.*, 1988, 1045.
- A. L. Wayda, I. Mukerji, J. L. Dye, and R. D. Rogers, *Organometallics*, 1987, **6**, 1328.
- T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc.*, 1964, **86**, 5194.
- M. J. Henderson and C. L. Raston, unpublished results.
- S. Harvey, P. C. Junk, C. L. Raston, and G. Salem, *J. Org. Chem.*, 1988, **53**, 3134.
- L. D. Quin, E.-Y. Yao, and J. Szewczyk, *Tetrahedron Lett.*, 1987, **28**, 1077.
- L. D. Quin, N. S. Rao, R. J. Topping, and A. T. McPhail, *J. Am. Chem. Soc.*, 1986, **108**, 4519.
- R. Appel, T. Gaitzsch, F. Knoch, and G. Lenz, *Chem. Ber.*, 1986, **119**, 1977.

<sup>‡</sup> *Synthesis and characterization:*  $\text{RPhCl}_2$ ; treatment of RH in thf with  $\text{Bu}^n\text{Li}$  in hexane (1.6 M) then  $\text{PCl}_3$  gave  $\text{RPhCl}_2$ ; m.p. 99–101 °C, decomp.; yield 86%; <sup>1</sup>H n.m.r. (300 MHz,  $\text{C}_6\text{D}_6$ ): δ 6.43 (m, 3H, pyridyl-CH), 7.10 (m, 10H,  $\text{C}_6\text{H}_5$ ), 8.11 (m, 1H, NCH); <sup>13</sup>C n.m.r. (75.5 MHz) δ 60.0, 122.9, 123.7, 125.1, 128.0, 135.9, 144.0, 147.1, 149.5, 165.2; <sup>31</sup>P n.m.r. (121.5 MHz) δ 169.2. (4); synthesis is given in Scheme 1; m.p. 116–119 °C; yield 37%; <sup>1</sup>H n.m.r. (300 MHz,  $\text{C}_6\text{D}_6$ ) δ 2.14 (m, 2H, PCH) 6.38 (m, 2H, PCHCH), 5.89 (m, 2H, PCHCHCH), 5.67 (m, 2H, PCHCHCHCH), 6.7–8.5 (m, 14H, aromatic-CH); <sup>31</sup>P n.m.r. (121.5 MHz) δ –122.0.

<sup>§</sup> *Crystal data* for  $\text{C}_{26}\text{H}_{22}\text{NP}$ , (4),  $M = 379.0$ , triclinic, space group  $P1$ ,  $a = 10.926(4)$ ,  $b = 10.199(3)$ ,  $c = 9.494(5)$  Å,  $\alpha = 95.00(3)$ ,  $\beta = 97.48(3)$ ,  $\gamma = 98.35(3)^\circ$ ,  $U = 1031.8(7)$  Å<sup>3</sup>,  $F(000) = 400$ ;  $Z = 2$ ,  $D_c = 1.22$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 1.5$  cm<sup>-1</sup>, 2701 unique diffractometer reflections ( $2\theta_{\text{max}} = 45^\circ$ ), 1649 with  $I > 3\sigma(I)$  used in the refinement,  $R = 0.069$ ,  $R_w = 0.061$ ,  $T = 295$  K. Anisotropic thermal parameter refinement for C, N, P. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.