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Preliminary communication

A SIMPLE ROUTE TO METALLA-2-INDANE-1,3-DIONES

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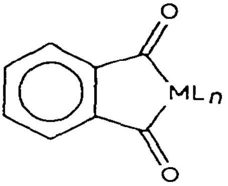
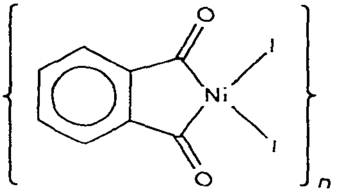
Summary

A simple and high yielding synthesis of metalla-2-indane-1,3-diones (phthaloyl metal complexes) by the insertion of low-valent transition metal complexes ($ClRh(PPh_3)_3$, $ClCo(PPh_3)_3$, $Fe(CO)_5$) into benzocyclobutenedione is reported. The structure of the rhodium complex was established by an X-ray analysis.

As part of a general project to explore the use of metallacycles as reagents in organic synthesis, we have been interested in the synthesis and chemistry of metalla-2-indane-1,3-diones (I) (phthaloyl metal complexes). Two such compounds have previously been described in the literature; however, the substrates and reaction conditions do not lend themselves to a rational, high yielding, and general approach to complexes of structure I. *ortho*-Diiodobenzene reacts with stoichiometric nickel tetracarbonyl to produce a polymeric nickel metallacycle (II) [1], while iron pentacarbonyl reacts with the same starting material under vigorous conditions to give a low yield of iron complex III [2]. Since low-valent transition metal species are known to insert into



(I)



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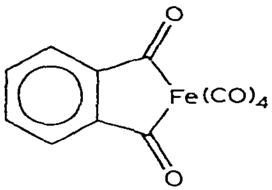
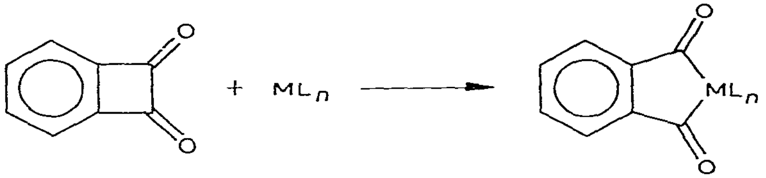


(III)



(1)

strained-ring organics [3] and specifically between α-dicarbonyls [4], we reasoned that reaction of benzocyclobutenedione with low-valent metals could provide a simple route to the desired complexes I (eq. 1).

Benzocyclobutenedione is known to react with $Pt(PPh_3)_4$ to give an adduct derived by insertion of a $Pt(PPh_3)_2$ unit between a carbonyl carbon and an aromatic ring carbon [5]; however, the system appeared worthy of further study with other metals.

Reaction of equimolar quantities of $ClRh(PPh_3)_3$ and benzocyclobutenedione in chlorobenzene at 110°C under N_2 lead to rapid disappearance of the dione (10 min, monitored by infrared). Cooling of the reaction at this stage gave an air-stable, yellow-orange, crystalline adduct A, m.p. 220—223°C, in 85% yield*; however, continued heating for 5 h caused conversion of A into an isomeric, air-stable, yellow compound B**, m.p. 250—252°C, which crystallized out of the reaction mixture in 93% yield upon cooling. Analytical data clearly showed both new compounds to be adducts of benzocyclobutenedione and a $ClRh(PPh_3)_2$ moiety, but they were distinctly different in their infrared and PMR spectra. Compound A showed multiple absorptions in the carbonyl region of the infrared at 1728, 1703 and 1670 cm^{-1} while compound B showed only one carbonyl absorption at 1645 cm^{-1}. In both complexes the NMR absorptions of the hydrogens on the non-PPh_3 aromatic ring were distinctly shielded relative to the PPh_3 absorptions. These four hydrogens appear as a complex multiplet between δ 7.07 and 6.68 ppm for complex A but as two very clean sets of doublets of doublets centered at δ 7.05 and 7.03 ppm for compound B***. These data lead one to the strong consideration that the $ClRh(PPh_3)_2$ moiety initially inserts into the benzocyclobutenedione ring in an unsymmetrical fashion to give structure IV as a kinetic product (compound A) which then isomerizes to the thermodynamically more stable V (compound B) as shown in eq. 2. Structural identification of IV rests upon its infrared similarity to the known platinum complex of analogous structure [5] and upon the isomerization of IV into V. The structure of complex V has been rigorously proven by a single-crystal X-ray diffraction study.

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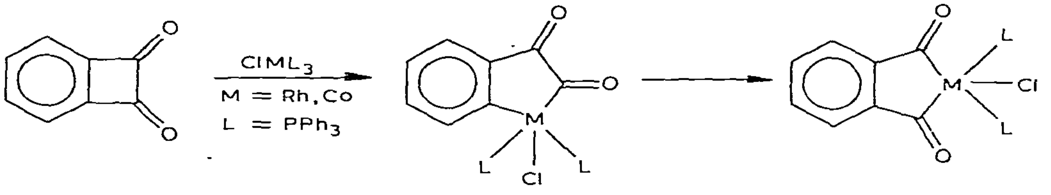
*IR (CH_2Cl_2) 1728, 1703, 1670 cm^{-1}, (KBr) 1729, 1697, 1671 cm^{-1}, 270 MHz NMR (acetone-d_6) δ (ppm) 7.78—7.15 (m, 35H, PPh_3), 7.07—6.68 (m, 4H); Anal. Found: C, 66.32; H, 4.35; Cl, 8.13. $RhC_{42}H_{34}ClP_2O_2 \cdot C_6H_5Cl$ calcd.: C, 66.14; H, 4.33; Cl, 7.82%. M.p. 220—223°C from chlorobenzene/hexane.

**IR (CH_2Cl_2) 1645 cm^{-1}, (KBr) 1645 cm^{-1}, 270 MHz NMR (acetone-d_6) δ (ppm) 7.72—7.50 (m, 12H), 7.44—7.15 (m, 18H), 7.05 (dd, 2H, J 5.7, 3.1 Hz), 7.03 (dd, 2H, J 5.7, 3.1 Hz); Anal. Found: C, 66.54; H, 4.56; Cl, 4.41. $RhC_{42}H_{34}ClP_2O_2$ calcd.: C, 66.47; H, 4.31; Cl, 4.46%. M.p. 250—252°C from chlorobenzene/hexane.

***The four hydrogens in question coincidently absorbed as a singlet at δ 6.91 ppm in $CDCl_3$; however, in acetone-d_6 the singlet resolved into the observed doublets of doublets. A brief attempt to distinguish compound A from B using CMR to look at the carbonyl carbons was unsuccessful due to the very long relaxation times of the carbonyl carbons. For example see ref. 7.



(2

(IV, M = Rh;
VI, M = Co)

(V, M = Rh;
VII, M = Co)

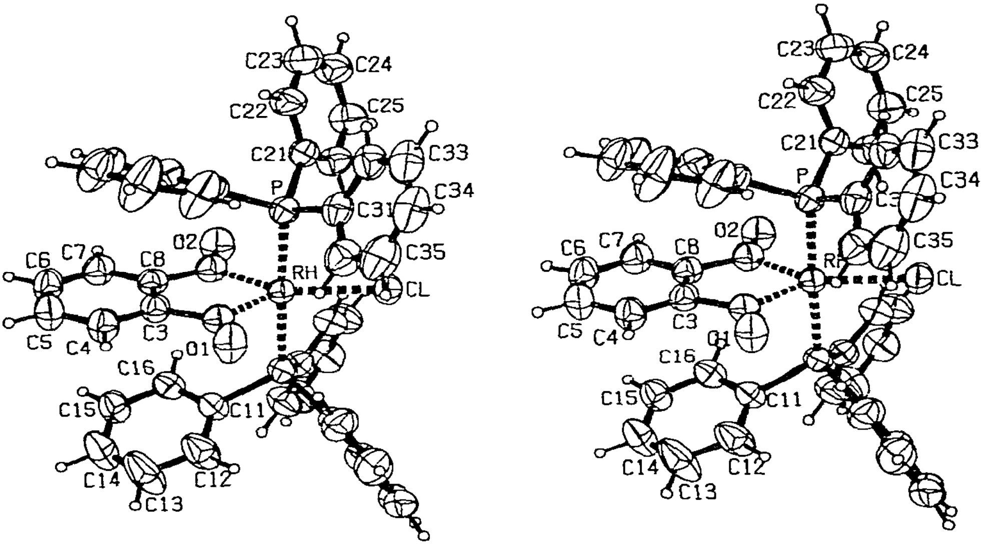


Fig. 1. Stereoscopic view of $Rh(PPh_3)_2Cl(C_8H_4O_2)$ showing the molecular geometry. The two PPh_3 groups are related to each other by reflection. For ring 1, the atom labels [C(11),···,C(16)] are shown next to the atoms related by the mirror symmetry (ring 1 is edge on in the drawing). Ring 2 is C(21),···,C(26) and ring 3 is C(31),···,C(36).

The results of the X-ray analysis*, shown in Fig. 1, confirm that V is a 5-coordinate, trigonal bipyramidal, rhodium(III) complex possessing the desired rhodia-2-indane-1,3-dione metallacycle. In the crystal, the molecules are located on mirror planes which pass through the $C_8H_4O_2RhCl$ moiety. The two PPh_3 groups of the molecules are related to each other by reflection. The atoms of each phenyl ring are coplanar to within ±0.01 Å and the P atom is significantly out of the planes of phenyl rings 1 (C(11),···,C(16) and 3 (C(31),···,C(36)). The intensity data were measured on a Hilger—Watts diffractometer (Ni filtered Cu-K_α radiation, θ—2θ scans, pulse height discrimination). A crystal measuring approximately 0.18 × 0.20 × 0.22 mm was used for data collection; the data were corrected for adsorption (μ = 55.9 cm^{-1}). A total of 2568 reflections were measured for $\theta < 57°$, of which 2216 we considered to be observed ($I > 2.5\sigma(I)$). The Rh, Cl and P atoms we located by direct methods [8] and the remaining nonhydrogen atoms were found on a series of electron density maps. Full matrix least squares was used for the refinement. In the final refinement anisotropic thermal parameters were used

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*$Rh(PPh_3)_2(Cl)(C_8H_4O_2)$: Orthorhombic, space group *Bbcm*, with *a* 16.471(2), *b* 18.611(3), *c* 24.129(3) Å, and d_{calcd} 1.427 g cm^{-3} for $Z = 8$ ($C_{44}H_{34}ClO_2P_2Rh$, M = 795.06).

for the heavier atoms and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations but their parameters were not refined. The final discrepancy indices are $R = 0.027$ and R_w 0.031 for the 2216 observed reflections. The final difference map has no peaks greater than ±0.6 eA^{-3}.

To study the generality of this metallacycle synthesis we have investigated the reaction of two other metals with benzocyclobutenedione. Treatment of equimolar quantities of benzocyclobutenedione and $ClCo(PPh_3)_3$ [6] in chlorobenzene at 110°C for 10 h led to disappearance of benzocyclobutenedione and formation of a brick-red, crystalline adduct $Co(PPh_3)_2(Cl)(C_8H_4O_2)$, m.p. 240—242°C in 90% yield*. The adduct gave the infrared spectrum almost superimposable on that of rhodium complex V and showed ν(CO) at 1635 cm^{-1}, while the PMR spectrum of the cobalt complex was identical in multiplicity and very similar in chemical shift to the rhodium complex. Based on these data we presume the cobalt complex to be isostructural with rhodium species V and to possess structure VII. During the early stages of the reaction, infrared monitoring showed the presence of a transient reaction product with ν(CO) at 1711 and 1685 cm^{-1} which could indicate the formation of cobalt complex VI in direct analogy with the rhodium reaction; however, VII does not build up to any appreciable concentration and we have not attempted to isolate this compound.

Finally, photolysis (150 watt GE flood lamp from 4 inches) of a benzene solution of benzocyclobutenedione and 4 equivalents of $Fe(CO)_5$ in a pyrex vessel for 5 h gave a 93% yield of the iron metallacycle III [2] (based on recovered benzocyclobutenedione).

The preparation of rhodium, cobalt, and iron metalla-2-indane-1,3-diones in very good yields indicates that this benzocyclobutenedione route to such metallacycles should be of general utility. We are currently exploring the scope of this reaction and investigating the synthesis of other metallacycles of synthetic potential via similar processes.

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References

1 N.A. Bailey, S.E. Hull, R.W. Jotham, S.F.A. Kettle, J. Chem. Soc. Chem. Commun., (1971) 282.
2 F.W. Grevels, J. Buchkremer, E.A. Koerner von Gustorf, J. Organometal. Chem., 111 (1976) 235.
3 K.C. Bishop III, Chem. Rev., 76 (1976) 461.
4 I.S. Kolomnikov, P. Svoboda, M.E. Vol'pin. Izv. Akad. Nauk, ser Khim., (1972) 2818; Chem. Abstr., 78 (1973) 97789k.
5 J.A. Evans, G.F. Everitt, R.D.W. Kemmitt, D.R. Russel, J. Chem. Soc. Chem. Commun., (1973) 158.
6 M. Aresta, M. Rossi, A. Sacco, Inorg. Chim. Acta, 3 (1969) 227.
7 E.R. Hamner and R.D.W. Kemmitt, J. Chem. Soc. Dalton Trans., (1971) 261.
8 G. Germain, P. Main and M.M. Wolfson, Acta Cryst. A, 27 (1971) 368.

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