Facile Displacement of an η^5-Indenyl Ligand. Crystal Structure of the $[Rh(Me_2PCH_2CH_2PMe_2)_2]^+$ Salt of the Naked Indenyl Anion

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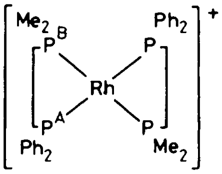
Reaction of $(\eta$-$C_9H_7)Rh(\eta$-$C_2H_4)_2$ with 2 equiv. of $Me_2PCH_2CH_2PMe_2$ (dmpe) or $Me_2PCH_2CH_2PPh_2$ results in displacement of all π-bound ligands; the salt $[Rh(dmpe)_2]^+[C_9H_7]^+$ has been characterized by *X*-ray crystallography.

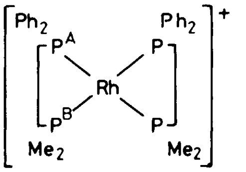
There has been considerable recent interest in the enhanced reactivity of η-indenyl transition metal complexes towards ligand substitution and related reactions compared with their η^5-C_5R_5 analogues.[1—4] This rate enhancement is believed to be related to the relative ease of ring slippage from η^5 to η^3.[1—4]

During the course of our investigation[5] of the factors affecting indenyl ring slip–fold distortions, we have found that both co-ordinated ethylene and η-indenyl ligands in $[(\eta$-$C_9H_7)Rh(\eta$-$C_2H_4)_2]$ (**1**)[2,3] are readily displaced by addition of $Me_2PCH_2CH_2PMe_2$ (dmpe) or $Me_2PCH_2CH_2PPh_2$. We report herein the isolation and structural characterization of the salt $[Rh(dmpe)_2]^+[C_9H_7]^-$ (**2**),‡ the first structurally characterized example of the 'naked' indenyl anion.

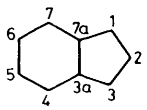
Addition of 2 equiv. of dmpe to (**1**) in tetrahydrofuran



(3a)



(3b)



Indenyl ring numbering for ^1H and ^{13}C n.m.r. spectroscopy

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‡ *Spectroscopic data* for (**2**): $^{31}P\{^1H\}$ n.m.r., 121.69 MHz (CD_3CN), δ 35.58 p.p.m. (d, $J_{Rh\text{-}P}$ 125 Hz); (C_5D_5N), 34.76 p.p.m. (d, $J_{Rh\text{-}P}$ 125 Hz); ^{13}C n.m.r., 75.59 MHz (C_5D_5N), δ 131.74 (m, C-3a, -7a), 119.02 (dt, $J_{C\text{-}H}$ 151, $^2J_{C\text{-}H}$ 5 Hz, C-2), 118.98 (dd, $J_{C\text{-}H}$ 151, $^2J_{C\text{-}H}$ 6 Hz, C-4, -7), 111.51 (dd, $J_{C\text{-}H}$ 152, $^2J_{C\text{-}H}$ 8 Hz, C-5, -6), 94.40 (dm, $J_{C\text{-}H}$ 157 Hz, C-1, -3), 29.07 (tm, $J_{C\text{-}H}$ 131 Hz, PCH_2CH_2P), 15.55 (qm, $J_{C\text{-}H}$ 130 Hz, PMe_2); $^{13}C\{^1H\}$ n.m.r., 75.59 MHz (CD_3CN), δ 93.4 (t, $J_{C\text{-}D}$ 24 Hz, C-1, -3); ^1H n.m.r., 300.57 MHz (CD_3CN), δ 7.18 (m, AA'BB', 2H, 4-, 7-H), 6.49 (s, br, 1H, 2-H), 6.29 (m, AA'BB', 2H, 5-, 6-H), 1.72 (m, 8H, PCH_2CH_2P), 1.45 (m, 24H, PMe_2); ^1H n.m.r. 300.57 MHz (C_5D_5N), δ 8.16 (m, AA'BB', 2H, 4-, 7-H), 7.60 (t, *J* 3.4 Hz, 1H, 2-H), 7.10 (m, AA'BB', 2H, 5-, 6-H), 6.99 (d, *J* 3.4 Hz, 2H, 1-, 3-H, 1.64 (m, 8H, PCH_2CH_2P), 1.39 (m, (24H, PMe_2). See H. P. Fritz and C. G. Kreiter, *J. Organomet. Chem.*, 1965, **4**, 198 for an analysis of the AA'BB' spin system (4-, 7-H and 5-, 6-H) in $Na[C_9H_7]$.

Spectroscopic data for (**3a**): $^{31}P\{^1H\}$ n.m.r., 121.69 MHz (C_5D_5N), δ 62.15 (dt $J_{Rh\text{-}P}$ 135, $^2J_{P\text{-}P}$ 32 Hz, P_A), 33.42 (dt, $J_{Rh\text{-}P}$ 122, $^2J_{P\text{-}P}$ 32 Hz, P_B); ^1H n.m.r., 300.57 MHz (C_5D_5N), δ 8.17 (m, AA'BB', 2H, 4-, 7-H), 7.75 [m, 8H, PPh_2(*ortho*)], 7.61 (t, *J* 3.4 Hz, 1H, 2-H), 7.57—7.50 [m, 12H, PPh_2 (*meta,para*)], 7.10 (m, AA'BB', 2H, 5-, 6-H), 7.10 (d, *J* 3.4 Hz, 2H, 1-, 3-H), 2.42 (br, 4H, Ph_2PCH_2), 1.45 (br, 4H, Me_2PCH_2), 0.90 (m, 12H, PMe_2). For (**3b**): $^{31}P\{^1H\}$ n.m.r., 121.69 MHz (C_5D_5N), δ 59.61 (dd, $J_{Rh\text{-}P}$ 131, $^2J_{P\text{-}P}$ 245 Hz, P_A), 34.79 (dd, $J_{Rh\text{-}P}$ 125, $^2J_{P\text{-}P}$ 245 Hz, P_B).

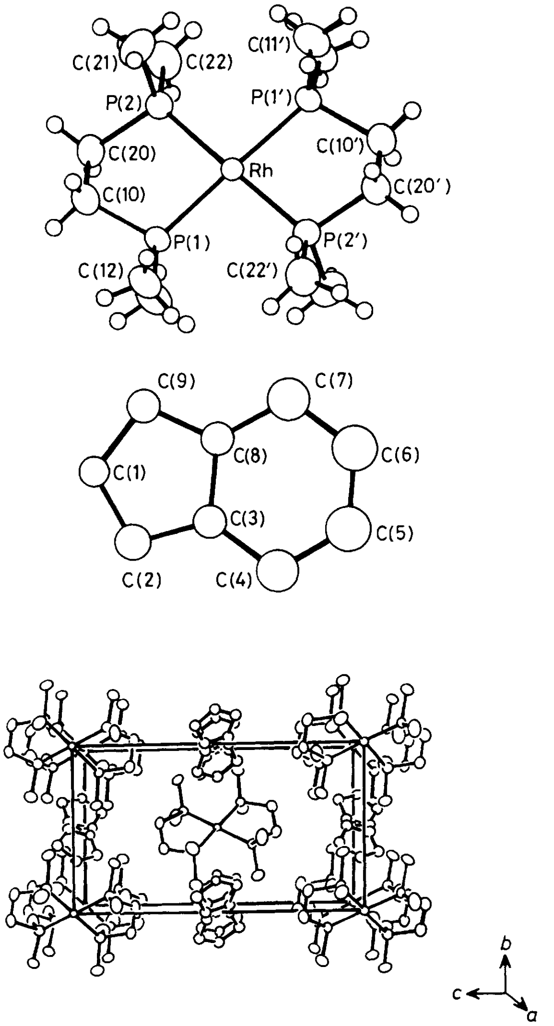

Figure 1. ORTEP views of (2) showing crystallographic numbering. The packing diagram shows only the five-membered ring of the disordered anion for clarity. Bond lengths (Å) and angles (°) for (2): Rh(1)–P(2) 2.277(1), Rh(1)–P(1) 2.287(1), P(1)–C(11) 1.814(4), P(1)–C(12) 1.821(4), P(1)–C(10) 1.842(4), P(2)–C(21) 1.804(6), P(2)–C(22) 1.812(4), P(2)–C(20) 1.844(4), C(10)–C(20) 1.494(6), C(1)–C(2) 1.37(1), C(1)–C(9) 1.40(1), C(2)–C(3) 1.38(1), C(3)–C(8) 1.40(1), C(3)–C(4) 1.47(1), C(4)–C(5) 1.43(2), C(5)–C(6) 1.33(2), C(6)–C(7) 1.39(2), C(7)–C(8) 1.37(2), C(8)–C(9) 1.49(1); P(1)–Rh(1)–P(1') 180.0, P(2)–Rh(1)–P(2') 180.0, P(2)–Rh(1)–P(1) 84.52(4), C(11)–P(1)–C(12) 102.2(2), C(11)–P(1)–C(10) 103.8(2), C(11)–P(1)–Rh(1) 115.9(2), C(12)–P(1)–C(10) 101.3(2), C(12)–P(1)–Rh(1) 122.7(2), C(10)–P(1)–Rh(1) 108.4(1), C(21)–P(2)–C(22) 103.0(3), C(21)–P(2)–C(20) 104.7(2), C(21)–P(2)–Rh(1) 115.5(2), C(22)–P(2)–C(20) 100.2(2), C(22)–P(2)–Rh(1) 122.4(2), C(20)–P(2)–Rh(1) 108.7(1), C(20)–C(10)–P(1) 109.8(3), C(10)–C(20)–P(2) 109.1(3), C(2)–C(1)–C(9) 113.8(7), C(1)–C(2)–C(3) 106.2(7), C(2)–C(3)–C(8) 110.5(7), C(2)–C(3)–C(4) 131.7(8), C(8)–C(3)–C(4) 117.8(8), C(5)–C(4)–C(3) 116(1), C(6)–C(5)–C(4) 122(1), C(5)–C(6)–C(7) 123(1), C(8)–C(7)–C(6) 117(1), C(3)–C(8)–C(9) 107.2(7), C(1)–C(9)–C(8) 102.3(7), C(7)–C(8)–C(9) 129.0(9), C(3)–C(8)–C(7) 123(1).

(THF) precipitates (2) in 98% yield. Likewise, addition of 2 equiv. of $Me_2PCH_2CH_2PPh_2$ to (1) in THF–hexane precipitates $[Rh(Me_2PCH_2CH_2PPh_2)_2]^+[C_9H_7]^-$ (3)‡ in 87% yield. The $^{31}P\{^1H\}$ n.m.r. spectrum of (3) shows a predominance of isomer (3a); only traces of (3b) are observed. The $^{31}P\{^1H\}$ n.m.r. spectrum of (2) in CD_3CN is identical to that of the salt $[Rh(dmpe)_2]Cl$ indicating that the $[Rh(dmpe)_2]^+$ and $[C_9H_7]^-$ ions are solvent-separated in solution. ^1H N.m.r. spectra of (2) in CD_3CN show rapid H/D exchange between H(1), H(3), and solvent as resonances are not observed for H(1) or H(3), and the signal for H(2) collapses to a singlet. All protons with appropriate couplings are observed in spectra recorded in $[^2H_5]$pyridine (C_5D_5N). The ^{13}C n.m.r. spectrum of (2) in C_5D_5N is very similar to that of $Li[C_9H_7]$ (4); the resonances for (2) are actually slightly downfield from those of (4), perhaps indicating some degree of ion pairing for (4) in solution.[6,7] The solid state structure of the salt $[(tmeda)Li]^+[C_9H_7]^-$ (tmeda = *N,N,N',N'*-tetramethylethylenediamine) shows significant interaction of the Li with all five carbons of the five-membered ring of the indenyl anion (av. Li–C 2.33 Å).[7]

$[(\eta\text{-}C_9H_7)Rh(\eta\text{-}C_2H_4)_2]$ **(1)**

$[Rh(dmpe)_2]^+[C_9H_7]^-$ **(2)**

$[Rh(Me_2PCH_2CH_2PPh_2)_2]^+ [C_9H_7]^-$ **(3)**

$Li^+[C_9H_7]^-$ **(4)**

$[(\eta\text{-}C_5H_5)Rh(\eta\text{-}C_2H_4)_2]$ **(5)**

The title compound (Figure 1) provides the first structurally characterized§ example of an indenyl anion which is not complexed to a metal. Other 'η^0' anions of the cyclopentadienyl type have been observed previously. The $[C_5(CO_2Me)_5]^-$ anion, stabilized by electron-withdrawing methoxycarbonyl substituents, has found utility as a counterion in the crystallization of a variety of cationic complexes.[9,10] More recently, Casey and co-workers published the first structure of the unco-ordinated parent cyclopentadienyl anion.[11] As expected this has approximate D_{5h} symmetry, the average C–C bond length being 1.399(8) Å and the C–C–C angle 108.0(5)°.

The choice of the space group $P2_1/n$ as the best model for the crystal structure analysis of (2) requires disorder of the planar indenyl anion about a crystallographic inversion centre. Thus, the 5- and 6-membered rings of the anion appear superimposed on each other in Fourier maps. Refinement of the indenide carbon atoms at half-occupancy and with isotropic thermal parameters gave a sensible geometry for the anion. The C–C bonds ranged between 1.33 and 1.49(2) Å, and angles about the 5-membered ring from 102.3(7) to 113.8(7)° and about the 6-membered ring from 116(1) to 131.7(8)°. A high degree of parameter correlation prevented successful anisotropic refinement of the anion, so that the e.s.d.s of the indenide C–C bond lengths and angles were not less than 0.01 Å and 0.7°, respectively. No significant

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§ *Crystal Data* for (2). $C_{15}H_{27}P_4Rh$, M = 434.2, monoclinic, space group $P2_1/n$ (non-standard setting of No. 14), a = 8.660(1), b = 9.124(1), c = 15.943(2) Å, β = 95.71(2)°, U = 1253.5(3) Å^3, Z = 2, D_c = 1.15 g cm^{-3}, $F(000)$ = 444 electrons, μ (Mo-K_α) = 9.15 cm^{-1}. Complex (2) crystallizes from MeCN–toluene as red blocks. Owing to the extreme moisture-sensitivity of the material, all manipulations were carried out in a glove box. A specimen of dimensions 0.4 × 0.3 × 0.2 mm was sealed in a glass capillary tube under a nitrogen atmosphere. The structure was solved by conventional techniques (Patterson, difference Fourier, full-matrix least-squares refinement).[8] For 2621 unique observed [$I > 3\sigma(I)$] reflections (ω scan method, $2\theta_{max.}$ 60°) collected on an Enraf-Nonius CAD4 diffractometer, the structure refined to R = 0.037, R_w = 0.051. The peaks of largest residual electron density (±1 electron Å^{-3}) were associated with the indenyl anion. 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.

improvement was observed upon extensive refinement in the acentric space group $P2_1$ ($R = 0.036$, $R_w = 0.049$) whereby the indenyl anion is not constrained to be 50 : 50 disordered about a crystallographic inversion centre. Parameter correlation persists in $P2_1$ and the slightly lower R values merely reflect the increased number of parameters being refined.

The shortest interionic C–C contact is 3.60 Å between C(4) of the indenide and C(11), one of the methyl carbon atoms of the cation, almost identical to that of 3.65 Å found for the closest C–C interionic contact in $[Re(NO)(Me)(PMe_3)_4][C_5H_5]$.[11]

The geometry of the $[Rh(dmpe)_2]$ cation is square planar. The Rh–P bonds are 2.277(1) and 2.287(1) Å, slightly shorter than the Rh–P bonds of 2.295(1) and 2.299(1) Å in $[Rh(PMe_3)_4]Cl$[12] which displays an out-of-plane distortion of the phosphine ligands by about 15° each.

Finally, we find[13] that excess dmpe will displace both ethylene and $C_5H_5^-$ from $[(\eta\text{-}C_5H_5)Rh(\eta\text{-}C_2H_4)_2]$ (**5**). The structure of the resulting salt $[Rh_2(dmpe)_4(\mu\text{-}dmpe)]^{2+}[C_5H_5]_2^-$ (current $R = 0.028$) and discussion of the relative rates of the reactions of dmpe with (**1**) and (**5**) will be reported elsewhere.

We thank Mr. B. C. West for skilled technical assistance and Dr. J. J. Mrowca for a sample of $Me_2PCH_2CH_2PPh_2$.

Received, 14th July 1986;¶ Com. 979

¶ Received in revised form 27th April 1987.

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