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Preliminary communication

THE ORGANOMETALLIC CHEMISTRY OF PHENALENE. NEUTRAL η^1, η^3 AND η^6 COMPLEXES OF PHENALENE

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Summary

The first η^1, η^3 and η^6 complexes of phenalene have been prepared and characterized. 1-Trimethylsilylphenalene was found to be a convenient precursor to di-μ-chlorobis(η^3-phenalenyl)dipalladium. The latter, when treated with two equivalents of triphenylphosphine, affords bis(triphenylphosphine)-η^1-phenalenylchloropalladium in good yield. η^6-Phenalenylchromium tricarbonyl was prepared in 21% yield from phenalene and $(CH_3CN)_3Cr(CO)_3$.

Recently we described the synthesis and properties of the first neutral and cationic η^2 complexes of phenalene (I) [1]. Prior to that report the only examples of phenalene complexes were the two η^3 platinum complexes of the ethoxyphenalenium ion [2]. The results of deuterium labelling studies on the rhodium promoted rearrangement of cycloprop[*a*]acenaphthylene, however, strongly suggest the intermediacy of a η^3-phenalenium rhodium complex [3]. We now wish to communicate the preparation and characterization of the first neutral η^1, η^3 and η^6 complexes of this unusual ligand.

Typically, η^3 complexes can be readily prepared from allyl halides. However, there are no known phenalene analogs, i.e., 1-halophenalenes, which could serve as entry points to η^3 complexes of I. Further limitations on approaches to these complexes were imposed when we found we could not adapt the olefin—Na_2PdCl_4—acetate buffer procedures recently employed by Jones [4] and Trost [5] for making π-allyl complexes to this ligand.

Encouraged by the successes of other groups [6] in using allylsilanes as intermediates for the synthesis of η^3-allylpalladium dimers, we prepared 1-trimethylsilylphenalene (II)*. The reaction of I with n-butyllithium in tetrahydrofuran (THF) followed by excess Me_3SiCl gave II, b.p. 125—130°C/0.8 torr, in 76% yield.

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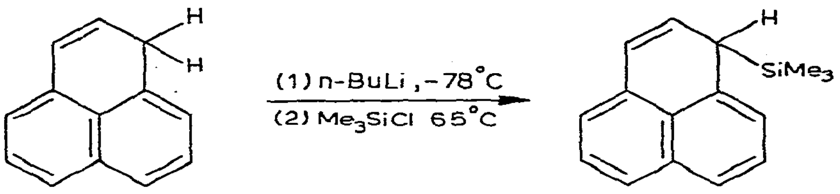
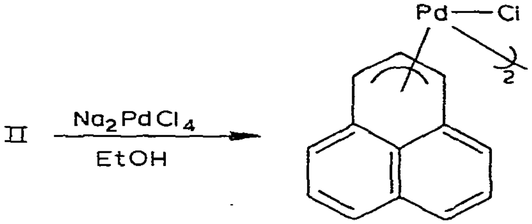
*Subsequent to our studies on II, another group has reported on its non-fluxionality [7].



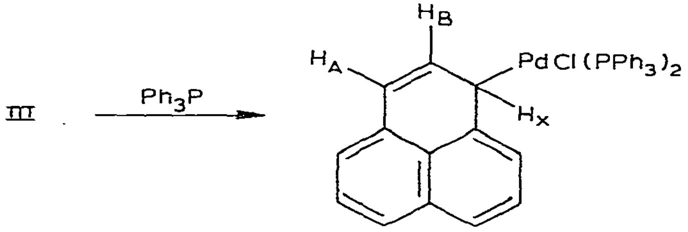
(I) (II)

The reaction of II with Na_2PdCl_4 in 95% ethanol gave the new complex III, an orange powder, m.p. 194—198°C in 90% yield. IR (Nujol): 425s; 368w; 285m cm^{-1}. UV ($CHCl_3$, $\lambda_{max}(\epsilon)$): 208 (4.07); 246 (4.03); 277 (3.62); 323 (3.53); 354 (3.65). Found: C, 50.55; H, 3.12; Pd, 34.91; Cl, 11.89. $[C_{13}H_9PdCl]_2$ calcd.: C, 50.85; H, 2.96; Pd, 34.65; Cl, 11.55%.



(III)

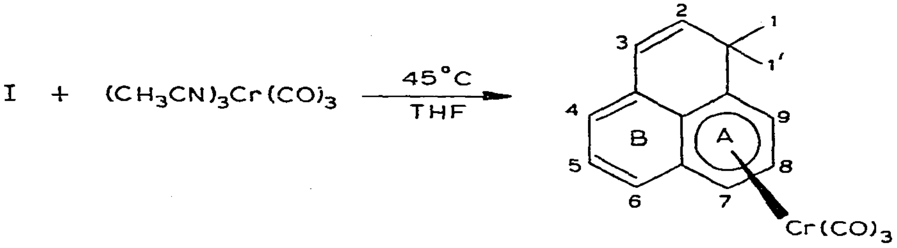
Di-μ-chlorobis(η^3-phenalenyl)dipalladium (III), similar to its indene [8] and triphenylmethane [9] analogues, is insoluble in common organic solvents ($\sim 10^{-4}$ g/ml) but quite soluble in dimethyl sulfoxide and pyridine. Both of these solvents cause extensive decomposition within an hour, generating the phenalenyl radical and ultimately the phenalene dimer [10]. However, the addition of triphenylphosphine dissolves III in chloroform completely when the ratio becomes 2/1 (Ph_3P/Pd). The PMR of this solution exhibits an ABX pattern at δ_A 6.78 (d, J_{AB} 9.6 Hz), δ_B 6.22 (doublet of doublets, J_{BX} 5.4 Hz) and δ_X 2.58 (broad doublet). This spectrum is consistent with the σ-bonded monomer IV.



(IV)

Evaporation of solvent and recrystallization from 1/1 CH_2Cl_2/C_5H_{12} at −78°C gave ~50% yield of orange crystals, m.p. 94—97°C; which were stable for <2 days at room temperature. Solutions of IV are also unstable at room temperature and the solvent must be removed immediately to isolate the compound.

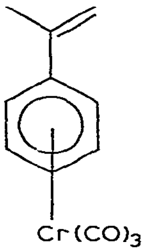
The first phenalene complex of the arene type, (η^6-phenalene)chromium tricarbonyl (V) was prepared in ~30% crude yield by treating I with $(CH_3CN)_3Cr(CO)_3$ in THF at 45°C for 5 h. The temperature is critical. Refluxing the mixture at 65°C for 2 h gave only a trace of product by TLC. A 21% yield of pure V, red crystals, m.p. 116—118°C, could be obtained by sublimation of chromatographed product (neutral alumina, 3/1 hexane/ether).



(V)

The pure sample is stable indefinitely at 0°C but shows some signs of decomposition after a day or two at room temperature. The infrared spectrum (Nujol) of V has carbonyl stretches at 1876s, 1901s and 1972s cm^{-1}. The mass spectrum gave peaks at m/e: 302 (M^+), 274, 246, 218 ($C_{13}H_{10}Cr^+$), 165 ($C_{13}H_9{}^+$), 136 ($Cr(CO)_3{}^+$), 52 (Cr^+). Our best elemental analysis gave C, 62.88; H, 3.64; Cr, 17.05. [$C_{16}H_{10}CrO_3$] calcd.: C, 63.58; H, 3.34; Cr, 17.20%.

The structural assignment is based largely on the PMR spectrum ($CDCl_3$). The uncomplexed protons H^5 and H^6 appear at δ 7.22—7.38, H^4 at δ 6.88 (d, J_{4-5} 6.9 Hz); H^7 at δ 5.85 (d, J_{7-8} 6.6 Hz); H^8 at δ 5.55 (t), H^9 at δ 5.32 (d, J_{8-9} 6.6 Hz); H^3 at δ 6.55 (d, J_{3-2} 10.5 Hz); H^2 at 6.15 (m); H^1 and $H^{1'}$ at 3.94 (broad singlet). In the uncomplexed ligand, H^1 absorbs at δ 4.07 and H^3 at δ 6.58. Complexation to ring A is indicated by the effect of the $Cr(CO)_3$ group on the methylene protons causing an upfield shift of 0.13 ppm. The chemical shift of the H^3 protons is practically unchanged in the complex. Typically, vinylic protons are shifted upfield by ~0.4 ppm when the $Cr(CO)_3$ moiety is coordinated to an attached benzene ring as in the styrene complex VI [11].



(VI)

Work on the extension of the coordination chemistry of phenalene and its derivatives to include complexes of larger metal atoms as well as complexes containing more than one metal is in progress.

Acknowledgment

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