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SYNTHESIS AND ELECTRONIC PROPERTIES OF THE NEUTRAL η^3-PHENALENYL PALLADIUM ACETYLACETONATE COMPLEX[1)]

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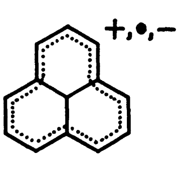
The first neutral η^3-phenalenyl acetylacetonate complex has been synthesized from the reaction of $[Pd(phenalenyl)Cl]_2$ with thallous acetylacetonate and its structure and electronic properties are discussed.

The phenalenyl ligand (**1**) possesses multicoordination mode possibilities in transition metal compounds. η^1-Phenalenyl[2a)] and related η^2-[2b)] and η^6-phenalene[2a)] complexes have so far been prepared, while the cationic platinum complex, $[Pt(PPh_3)_2(6\text{-ethoxyphenalenyl})]^+$ (**2**), was single example of the well-characterized η^3 structure.[3)] The presence of the nonbonding molecular orbital (NBMO) is common to odd alternant hydrocarbons. It is the NBMO of the phenalenyl, (**3**), that might play an important role in η^3-phenalenyl-metal bonding on the analogy of the well-established $[Pd(\pi\text{-allyl})X]_2$ type complexes. We herein describe the synthesis and characterization of Pd(acac)-(phenalenyl), (**4**), which turns out to be the first neutral complex having an η^3 mode of unsubstituted phenalenyl (**1**).



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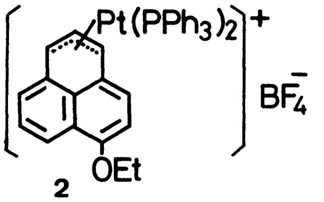

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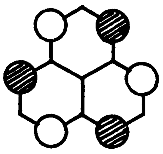

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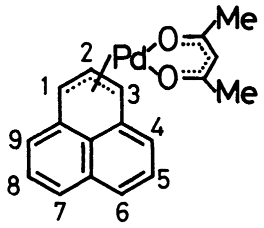

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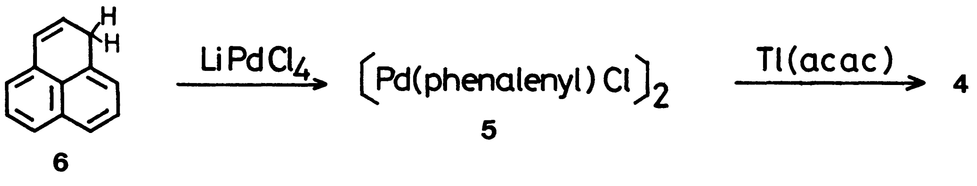
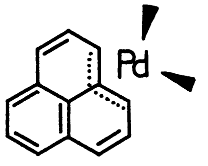
Although di-μ-chlorobis(phenalenyl)palladium (**5**) was already prepared by two-step procedure, its structural detail has yet been unknown owing to a lack of the NMR data because of its insolubility and/or lability in common NMR solvents.[2a)] We selected **5** as a precursor for the synthesis of a simpler η^3-unsubstitued phenalenyl-palladium complex. First the complex **5** was prepared by one-step procedure[4)] : reaction of phenalene (**6**) with lithium tetrachloropalladate led to the precipitation of **5**[5)] in 90% yield. Then, treatment of a solution of **5** in benzene with thallous acetylacetonate[6)] gave brownish green precipitates in 50-60% yield after reprecipitation from benzene-hexane. The product has been characterized as **4** on the basis of the elemental analysis and



^{1}H NMR spectrum, δ (CD_2Cl_2, at -10°C) 7.94, 7.90 (4H, AB part of an ABK, J_{AB} = 0.9 Hz, H-4,6,7,9), 7.31 (2H, K part of an ABK, J_{AK} = 7.4, J_{BK} = 8.3 Hz, H-5,8), 6.11 (1H, A part of an AB_2, J_{AB} = 6.6 Hz, H-2), 5.96 (2H, B part of an AB_2, H-1,3), 5.18 (1H, s, C-H of acetylacetonate), and 1.83 (6H, s, C-CH_3). Six protons (ABK system) in the lower field and three protons (AB_2 system) in the higher field of the aromatic resonances clearly support the structure **4**.

The other η^3 structure **7** might also be a possibility besides the observed geometry **4**, because the two types of Pd coordinations are topologically equivalent with respect to the NBMO-Pd interaction. Extended Hückel calculations were then performed on **4** and **7**.$^{7)}$ The structure of **4** was computed to be more stable than that of **7** in harmony with the result of our NMR study and with the structure of the analogous Pt complex (**2**). However, the difference in stability between the two geometries amounts to merely 1.2 kcal/mol. This is because the major energy gain for both **4** and **7** indeed originates from the phenalenyl(NBMO)(**3**)-Pd(b_2)(**8**) interaction. Perhaps there will be a good chance of reversing the relative stability by, e.g., choosing a suitable substituent at the phenalenyl skeleton. It would be an interesting experimental as well as theoretical target to find what sort of chemical modification makes it possible to isolate a molecule of the structure (**7**).



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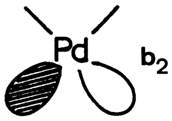

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The fluxional behavior of (**4**) e.g., the haptotropic shift of Pd(acac) from one ring to another, if occurs, would proceed *via* **7** in view of its stability. There was, however, no evidence in the ^{1}H NMR spectrum for the appearance of a dynamic process up to its decomposition temperature, +60°C.

References

1) The Chemistry of Phenalenium Systems. 37. For part 36, Y. Sugihara, K. Hashimoto, and I. Murata, submitted for publication.

2) a) S. Lin and P. Boudjouk, *J. Organometal. Chem.*, 1980, 187, C11; b) J. B. Woell and P. Boudjouk, *J. Organometal. Chem.*, 1979, 172, C43.

3) A. Keasey, P. M. Bailey, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1978, 142.

4) H. C. Volger, *Recl. Trav. Chim. Pays-Bas*, 88, 225 (1969).

5) Precipitates (**5**) afforded the proper combustion analysis.

6) S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 1963, 4806.

7) The geometries **4** and **7** were roughly optimized, where the Pd(acac)$^+$ plane was assumed to stand perpendicular to the phenalenyl plane with the Pd-phenalenyl plane distance of 1.7 Å.
The strategy is very close to the way in whcih Albright and his collaborators have analyzed haptotropic rearrangements of an extensive series of polyene-ML_n complexes. (T. A. Albright, P. Hofmann, R. Hoffmann, C. P. Lillya, and P. A. Dobosh, *J. Am. Chem. Soc.*, 105, 3396 (1983)). We thank Professor Albright for providing a preprint of his paper prior to publication. Atomic parameters of Pd are as follows. H_{ii}: 5s, -7.32 eV; 5p, -3.75 eV; 4d, -12.02 eV. Orbital exponents: 5s, 2.190; 5p, 4d, 5.983 (0.5264)+2.613 (0.6373). Detailed results will be reported elsewhere.

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