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Coordination of Polycyclic Conjugated Hydrocarbons to Palladium. Syntheses, Characterization, and Molecular Orbital Study of Pd(η^3-phenalenyl)(acac) and [Pd(η^3-indenyl)Cl]$_2$

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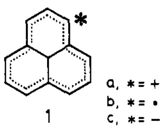
Pd(η^3-phenalenyl)(acac) (**15**) has been prepared by a two-step procedure from phenalene and [Pd(η^3-indenyl)Cl]$_2$ (**17**) by a one-step from indene directly. These two palladium complexes are the rare examples of polycyclic conjugated hydrocarbons coordinated to Pd in an η^3 manner, which were characterized successfully by NMR spectra. Extended Hückel molecular orbital calculations were performed on **15** and Pd(indenyl)(acac), a model of **17**, in several possible geometrical variations. Their most theoretically stable structures coincide with what were established by the present NMR analysis. We discuss the nature of the Pd–polyene bonds, fluxionality, and a possible geometrical isomer of **15**, yet another η^3 structure.

Introduction

Phenalenyl (**1**) possesses a nonbonding molecular orbital (NBMO) (**2**) as a common feature of odd alternant hydrocarbons.[2] Since the NBMO can be either doubly occupied, singly occupied, or vacant, the corresponding three oxidation states of phenalenyl (**1a–c**) are all expected to be stable. In fact, the successful syntheses and characterization of these species have appeared.[3] Taking advantage of the versatile redox property of phenalenyl, a novel polycyclic hydrocarbon, pentaleno[1,2,3-*cd*:4,5,6-*c′d′*]diphenalene, has recently been shown to be a highly amphoteric redox hydrocarbon.[4]



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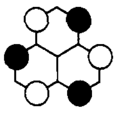

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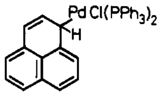
Naturally, this has been extended to the transition-metal complexes of phenalene. Of particular interest have been multicoordination mode possibilities of the polycyclic conjugated ligand. The phenalenyl ligand may coordinate to a metal in either an η^1-σ-allyl (**3**),[5] η^2-π-alkene (**4–6**),[6] η^3-π-allyl, or η^6-π-arene (**7**)[5] fashion, mainly developed by Boudjouk and his co-workers. It is in the (η^3-phenalenyl)metal bonding that the NBMO might play a crucial role in the analogy of familiar Pd–π-allyl interactions.[7] A single example of the well-characterized η^3 structure was the cationic platinum complex **8** reported by Maitlis and his co-workers.[8] Although bis(μ-chloro)-bis(η^3-phenalenyl)palladium (**10**) was also prepared,[5] its structural detail has yet been unknown because of its insolubility and/or lability in common NMR solvents. Another interesting feature characteristic of phenalenyl complexes includes the ability of metal fragments to migrate in the phenalenyl plane. This is exemplified by the thermally and photochemically induced sigmatropic shifts of the trimethylsilyl group in **9** reported by Pagni et al.[9]



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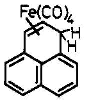

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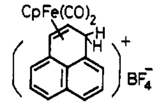

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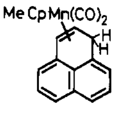

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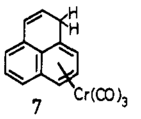

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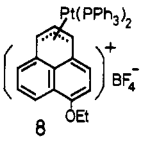

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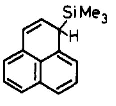

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We herein describe an extension of the η^3 mode ligand in palladium complexes to polycyclic conjugated hydrocarbons. Thus, the neutral unsubstituted phenalenyl (**15**)[10] and indenyl (**17**) complexes have been prepared and characterized by NMR spectroscopy. In addition, we carried out extended Hückel MO calculations on these complexes to elucidate the electronic structures and bonding, with parameters specified in the Appendix.

Results and Discussion

When phenalenyl binds to a metal through an η^3 fashion, we expect two different coordination types such as C$_1$–C$_2$–C$_3$ (**11**) and C$_3$–C$_{3a}$–C$_4$ (**12**), since the coefficients of the

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[1] (a) Department of Chemistry. (b) Department of Macromolecular Science.

[2] (a) Reid, D. H. *Q. Rev., Chem. Soc.* **1965**, *19*, 274. (b) Murata, I. "Topics in Non-Benzenoid Aromatic Chemistry"; Nozoe, T., Breslow, R., Hafner, K., Ito, S., Murata, I., Eds.; Hirokawa: Tokyo, 1973; Vol. 1, p 159. (c) Haddon, R. C. *Nature (London)* **1975**, *256*, 394; *Aust. J. Chem.* **1975**, *28*, 2343.

[3] (a) Pettit, R. *Chem. Ind. (London)* **1956**, 1306; *J. Am. Chem. Soc.* **1960**, *82*, 1972. (b) Reid, D. H. *Chem. Ind. (London)* **1956**, 1504. (c) Boekelheide, V.; Larrabee, C. E. *J. Am. Chem. Soc.* **1950**, *72*, 1245.

[4] Nakasuji, K.; Yoshida, K.; Murata, I. *J. Am. Chem. Soc.* **1983**, *105*, 5136.

[5] Lin, S.; Boudjouk, P. *J. Organomet. Chem.* **1980**, *187*, C11.

[6] Woell, J. B.; Boudjouk, P. *J. Organomet. Chem.* **1979**, *172*, C43.

[7] The bonding between π-allyl and d^8 transition metals have been occasionally investigated. Some examples, which are not necessarily for Pd, are as follows: (a) Albright, T. A.; Hoffmann, R.; Tse, Y.-C.; D'Ottavio, T. *J. Am. Chem. Soc.* **1979**, *101*, 3812. (b) Böhm, M. C.; Gleiter, R. *Angew. Chem.* **1983**, *95*, 334. (c) Böhm, M. C.; Gleiter, R.; Batich, C. D. *Helv. Chim. Acta* **1980**, *63*, 990 and references therein. (d) Rohmer, M.-M; Demuynck, J.; Veillard, A. *Theor. Chim. Acta* **1974**, *36*, 93. (e) Sakaki, S.; Nishikawa, M.; Ohyoshi, A. *J. Am. Chem. Soc.* **1980**, *102*, 4062.

[8] Keasey, A.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1978**, 142.

[9] Butcher, J. A., Jr.; Pagni, R. M. *J. Am. Chem. Soc.* **1979**, *101*, 3997.

[10] For a preliminary communication, see: Nakasuji, K.; Yamaguchi, M.; Murata, I.; Tatsumi, K.; Nakamura, A. *Chem. Lett.* **1983**, 1489.

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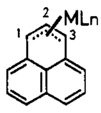
Table I. Extended Hückel Parameters in the Calculations

orbital		H_{ii}, eV	orbital exponents[a]
Pd	4d	−12.02	5.983 (0.5264) + 2.613 (0.6373)
	5s	−7.32	2.190
	5p	−3.75	2.152
C	2s	−21.4	1.625
	2p	−11.4	1.625
O	2s	−32.30	2.275
	2p	−14.80	2.275
H	1s	−13.60	1.30

[a] For the Pd d function a double-ζ expansion was used. The normalized expansion coefficients are given in parentheses.

NBMO (2) are topologically equivalent. Furthermore, the third geometry (13) can also be drawn by using the classical resonance structure.



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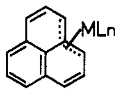

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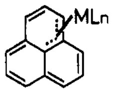

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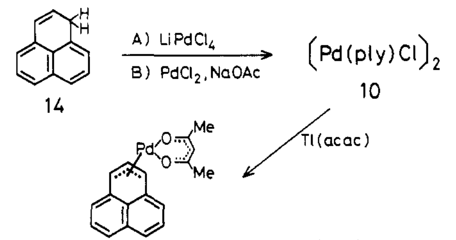
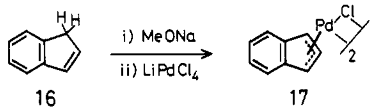
We selected **10** as a precursor for the preparation of a simpler η^3-unsubstituted phenalenylpalladium complex, although detail of its structure was not known. We adopted the Volger[11] or the Hüttel[12] procedure to convert phenalene (**14**) into **10** directly, by taking into account the mechanism proposed for the formation of (π-allyl)palladium complexes from olefins[11,13] and the presence of a weak, allylic and benzylic C–H bond in **14**. Thus **10** was prepared by a one-step procedure: treatment of **14** with lithium tetrachloropalladate (method A) or with palladium chloride in the presence of sodium acetate (method B) led to the precipitation of **10**[14] in 90% yield. Method A is recommended for the preparation of **10**. We successfully converted **10** into a neutral (η^3-phenalenyl)palladium acetylacetonate complex (**15**) by applying the Robinson and Shaw procedure.[15] Treatment of **10** with thallous acetylacetonate in benzene afforded brownish solids that are expectedly soluble in common organic solvents. It could be handled at room temperature for the spectroscopic measurements, but the solids stored decomposed gradually within 10 days even at −78 °C. The product has been characterized as the molecular structure **15** on the basis of elemental analysis and ^{1}H NMR data (100 MHz): δ (CD_2Cl_2, at −10 °C) 7.94, 7.90 (4 H, AB part of an ABK, J_{AB} = 0.9 Hz, H-4,6,7,9), 7.31 (2 H, K part of an ABK, J_{AK} = 7.4, J_{BK} = 8.3 Hz, H-5,8), 6.11 (1 H, A part of an AB_2, J_{AB} = 6.6 Hz, H-2), 5.96 (2 H, B part of an AB_2, H-1,3), 5.18 (1 H, s, C–H of acetylacetonate), 1.83 (6 H, s, C-CH_3). Such a simple pattern in its ^{1}H NMR spectrum is consistent with the structure of the phenalenyl moiety having C_{2v} molecular symmetry, **11** or **12** (ML_n = Pd(acac)). Six protons in the lower field and three protons in the higher field of the aromatic resonances unambiguously support structure **15** that contains the coordination type **11**.



Indenyl also includes a π-allyl moiety in its π-electron system. Although attempts to characterize the indenylpalladium complex **17** were reported, the nature of the bonding was described with some ambiguity.[16] We applied a modified Volger procedure for the preparation of **17**.



Treatment of indene in methanol with sodium methoxide and then with lithium tetrachloropalladate gave **17** in 84% yield. In contrast to the instability of **15**, complex **17** can be stored at room temperature and is stable even in dimethyl sulfoxide and pyridine. Its structural assignment is based on elemental analysis and ^{1}H and ^{13}C NMR data. The η^3 mode of the indenyl ligand in **17** giving C_{2v} molecular symmetry is characterized by NMR spectroscopy. The ^{1}H NMR (90 MHz) spectrum in Me_2SO-d_6 shows an AA′BB′ system, at δ 7.08 (center of the signals), for the six-membered ring protons and an AX_2 system, at δ 6.99 (t, 1 H, J = 3 Hz, H-2) and 6.30 (d, 2 H, J = 3 Hz, H-1,3), for the five-membered ring protons. Furthermore, the ^{13}C NMR spectrum consists of only five resonances, at δ 85.4 (C-1), 114.0 (C-2), 127.4 (C-4), 118.8 (C-5), and 136.9 (C-3a).

The attempted study to detect the fluxional behavior of the η^3 complexes was performed. The haptotropic shift of Pd(acac) from one ring to another in **15**, if it occurs, would proceed via **12** (ML_n = Pd(acac)). 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.[17] From the theoretical study (vide infra) no haptotropic rearrangement is expected in the indenyl complex, and **17** is indeed fairly stable at as high as +110 °C. Clearly, the synthesis of thermally more stable complexes (involving the change of ligand etc.) is needed to observe the haptotropic shift of the metal around the phenalenyl ring.

Theoretical Studies

The major purpose in this section of the study is not to search for accurate geometries of stable and metastable structures. Instead, our attention is directed to outlining the electronic details of the bonding for palladium polycyclic conjugated systems, focusing on these issues: what sort of interactions do exist between orbitals of Pd(acac) and those of the polyenes and how do the interactions vary depending on a choice of coordination sites.

We first consider the coordination modes of Pd(acac) to phenalenyl. A useful approach would be to divide the molecule into Pd(acac)$^+$ and (phenalenyl)$^-$, though the choice is only a matter of formality and does not affect our theoretical analysis. The metal-centered frontier orbitals of a d^8 Pd(acac)$^+$ fragment are simple derivatives of a square-planar system, as shown in **18**.[18] A block of four

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[11] Volger, H. C. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 225.

[12] Hüttel, R.; Kratzer, J.; Bechter, M. *Chem. Ber.* **1961**, *94*, 766.

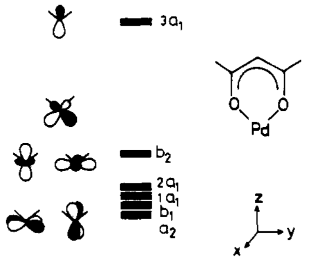
[13] Trost, B. M.; Strege, P. E.; Weber, L.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3407.

[14] Precipitates (**10**) afforded the proper combustion analysis.

[15] Robinson, S. D.; Shaw, B. L. *J. Chem. Soc.* **1963**, 4806.

[16] Samuel, E.; Bigorgne, M. *J. Organomet. Chem.* **1969**, *19*, 9.

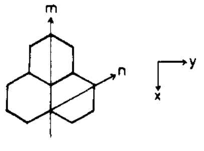
[17] The possibility for the intermediacy of an η^3-phenalenyl rhodium complex and for the migration of the metal has been suggested during the rearrangement of cycloprop[*a*]acenaphthylene in the presence of a catalytic quantity of rhodium dicarbonyl chloride dimer by Paquette et al., see: Paquette, L. A.; Gree, R. *J. Organomet. Chem.* **1978**, *146*, 319.



18

occupied levels, $a_2(xy)$, $b_1(xz)$, $1a_1(z^2)$, and $2a_1(x^2 - y^2)$, are at low energy, which are primarily made up of Pd d orbitals. In the somewhat higher vacant level (b_2), Pd d_{yz} is hybridized with Pd p_y in such a way that the orbital lobes point away from the acac ligand. At even higher energy is $3a_1$, consisting of Pd s and p_z orbitals.

The $Pd(acac)^+$ fragment carries twelve valence electrons around Pd: eight d electrons plus four electrons from $(acac)^-$. Thus the coordination of $Pd(acac)^+$ is likely to occur only to the π-allyl portion of the phenalenyl anion, forming an η^3 mode complex of $[Pd(\pi\text{-allyl})X]_2$ with a 16-electron count. In order to find stable η^3 coordination sites on phenalenyl, we examined how the potential energy curve evolved when $Pd(acac)^+$ was shifted along the *m* or *n* axis in **19**. The planar geometry of the phenalenyl skeleton as well as all of the C–C distances of 1.41 Å were unchanged during the shift. The $Pd(acac)^+$ plane was assumed to stand perpendicular to the *m* or *n* axis and thus to the phenalenyl plane, while the Pd–phenalenyl plane distance was held constant at 1.7 Å. The strategy employed here is very close to the way in which Albright and his co-workers have analyzed haptotropic rearrangements of an extensive series of (polyene)ML_n complexes.[19]



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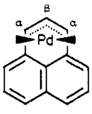
Three potential minima were found, each of which corresponds to the coordination type **11**, **12**, or **13**.

The total energies computed for the three isomers are compared in **20**–**22**, where the most stable one is **20** in harmony with the structure of **15** determined by our NMR study and with that of the analogous Pt complex **8**. Coordination type **22** is less stable than **20** by 15.7 kcal/mol but may be important when we examine the pathways of a Pd(acac) scramble on the phenalenyl ring as will be discussed elsewhere. However, the most intriguing aspect of the energy scheme is that it suggests the existence of **21** under certain conditions.



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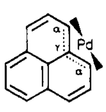

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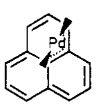

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ΔE (kcal/mol) 0.0 1.2 15.7

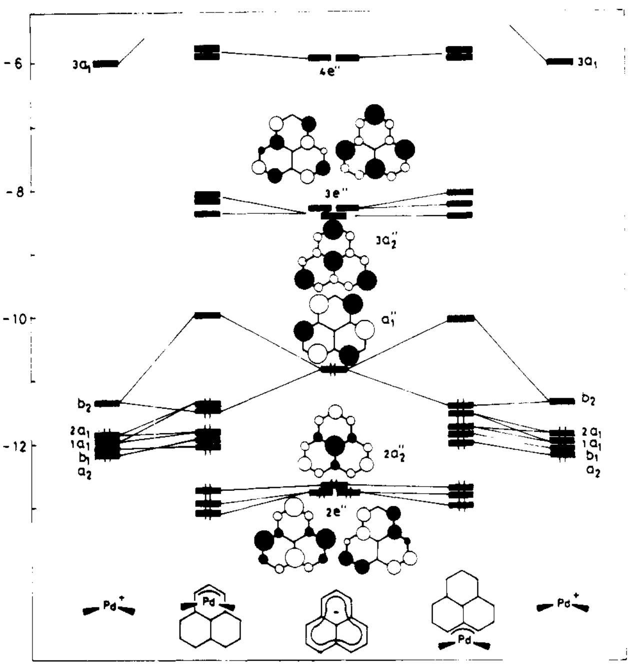

Figure 1. Interaction diagrams for the valence orbitals of $(phenalenyl)^-$ and $Pd(acac)^+$ in the geometry **20** (left) and **21** (right). At the middle, phenalenyl anion carries seven frontier orbitals, while the rest of high-lying π* and low-lying π orbitals are not shown.

Here we discuss the bonding of $Pd(acac)^+$ with the phenalenyl anion in relation to structures **20** and **21**. Figure 1 shows the interaction diagram for the two coordination types, **20** at the left and **21** to the right. The phenalenyl ring bears 13 π and π* orbitals. In the middle of the figure, we depict only seven frontier orbitals from a top view. The rest of the high-lying π* and low-lying π orbitals are practically innocent of interaction with $Pd(acac)^+$ and are omitted from the figure. The occupied 2e″ and $2a''_2$ orbitals nearly degenerate in our calculation. A mirror image of these corresponds to the set of unoccupied $3a''_2$ and 3e″ orbitals. The NBMO level, being assigned to a''_1, locates in between these three orbital sets and is doubly occupied if we view phenalenyl as an anionic ligand.

It is the NBMO that finds a pronounced interaction with the b_2 orbital of $Pd(acac)^+$. Because of the D_{3h} molecular symmetry, the NBMO is delocalized equally over the six α-carbon atoms of phenalenyl with an alternate phase. The topology provides for good overlap with Pd on both coordination sites, **20** and **21**. This is why the stability of the two geometries is nearly balanced. The calculated overlap populations between NBMO and b_2 are 0.163 for **20** and 0.162 for **21** and confirm the above argument. The importance of NBMO in the Pd(acac)–phenalenyl bond contrasts with the less pronounced role of the orbital being found in the (phenalenyl)$Cr(CO)_3$ cation.[19]

The calculated difference in energy between **20** and **21** is slight, favoring the former structure. There is a good chance of reversing the relative stability by, for example, 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 enables us to isolate a molecule of structure **21**.

We now turn to the indenyl complex **17**. In our theoretical analysis, Pd(indenyl)(acac) (**23**) instead of **17** is selected as a model complex and regarded as a combination of $Pd(acac)^+$ and the indenyl anion as we did for **15**. It is possible to coordinate a π-allyl anion within the indenyl

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[18] The molecular orbitals of an ML_2 fragment in C_{2v} geometry have been described in the literature. (a) Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1977**, 602. (b) Hofmann, P. *Angew. Chem.* **1977**, *89*, 551. (c) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801. (d) Yoshida, T.; Tatsumi, K.; Otsuka, S. *Pure Appl. Chem.* **1980**, *52*, 713. (e) Tatsumi, K.; Hoffmann, R. *Inorg. Chem.* **1981**, *20*, 3771.

[19] Albright, T. A.; Hofmann, P.; Hoffmann, R.; Lillya, C. P.; Dobosch, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 3396.

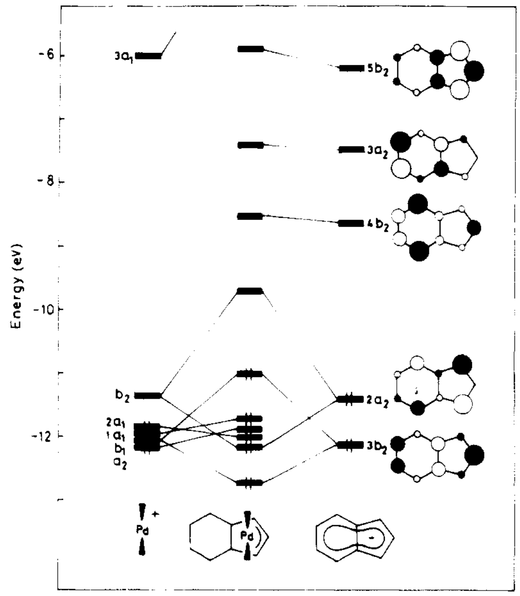
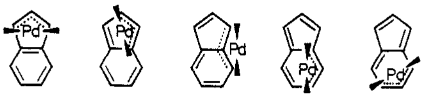


Figure 2. Interaction diagrams for the valence orbitals of (indenyl)$^-$ and Pd(acac)$^+$. The highest π^* and three low-lying π of (indenyl)$^-$ are omitted from the figure.

π system in five distinct ways (**24**–**28**). The relative energies calculated for these isomers are given below in **24**–**28**. It is evident that the molecule favors the geometry **24**, which accords with the experimental finding and qualitative consideration.



	24	25	26	27	28
ΔE (kcal/mol)	0.0	+ 20.0	+ 13.6	+ 17.5	+ 16.4

An interaction diagram for **24** is constructed in Figure 2. The indenyl anion has nine π and π^* orbitals, five of which appear on the right side of the figure in the energy range of −13 to −5 eV. The major energy gain originates from a bonding interaction between the low-lying empty b_2 orbital of palladium and the highest occupied orbital of the indenyl anion $2a_2$. The second highest orbital $3b_2$ also finds a match with the Pd b_1 orbital while the Pd $1a_1$ and $2a_1$ orbitals mix into the interaction in a somewhat complicated way. However, the orbitals are all occupied and the net effect is destabilizing.

The strong b_2(Pd)–$2a_2$ bonding interaction is present in structure **24** only. This is due to the orbital shape that $2a_2$ possesses and results in a heavy geometrical preference of **24** over the others. The overlap populations calculated for the b_2–$2a_2$ pair support the analysis, being 0.237 (**24**), 0.019 (**25**), 0.147 (**26**), 0.045 (**27**), and 0.092 (**28**).

Experimental Section

General Data. All the melting points are uncorrected. Infrared spectra and ultraviolet spectra were recorded on Hitachi EPI G21 and Hitachi 340 spectrophotometers, respectively. Proton NMR spectra were measured at 100 and 90 MHz by using Varian XL-100-15 and JEOL FX90Q spectrometers, respectively, and carbon-13 NMR spectrum was measured at 22.5 MHz by using a JEOL FX90Q instrument. All chemical shifts are reported in parts per million (δ) relative to internal Me_4Si, and coupling constants (J) are given in hertz. All reactions were performed under a nitrogen atmosphere.

Bis(μ-chloro)bis(phenalenyl)dipalladium Type Complex (10). Method A. To a solution of phenalene **14** (0.171 g, 1.03 mmol) in methanol (15 mL) and water (15 mL) was added a solution of Li_2PdCl_4 (0.297 g, 1.35 mmol) in methanol (20 mL) at room temperature. After the solution was stirred overnight, the resulting orange precipitates were collected by filtration, washed with methanol and ether, and dried under reduced pressure to yield 0.291 g (92%) of **10**; mp (decomp) >180 °C. Anal. Calcd for $C_{26}H_{18}Pd_2Cl_2$: C, 50.85; H, 2.95; Cl, 11.55. Found: C, 51.15; H, 3.08; Cl, 11.95.

Method B. To a solution of **14** (0.10 g, 0.6 mmol) in ethanol (10 mL) cooled in an ice bath was added a solution of $PdCl_2$ (0.089 g, 0.5 mmol) and sodium acetate (0.250 g, 3 mmol) in 50% acetic acid (8 mL) and stirred for 1 h. After the solution was stirred for 2 h at room temperature, the resulting precipitates were collected by filtration, washed with ethanol and ether, and dried under reduced pressure to yield 0.120 g (80%) of **10**. A second crop (0.02 g, 13%) of **10** was obtained from the filtrate.

(Acetylacetonato)(η^3-phenalenyl)palladium(II) (15). To a suspension of **10** (0.112 g, 0.183 mmol) in benzene (10 mL) was added in one portion a hot solution of thallous acetylacetonate (0.110 g, 0.365 mmol) in benzene (20 mL) at room temperature, and the solution was stirred for 0.5 h. A small amount of insoluble material was filtered off, and the filtrate was evaporated to dryness under reduced pressure. The residue was dissolved in benzene, and to the solution was added hexane to precipitate **15** as a brown solid (0.080 g, 59%): mp (decomp) <140 °C; ^1H NMR, see text; IR (Nujol) 373, 415, 432, 592, 617, 640, 655, 675 cm^{-1}, (KBr) 1580 cm^{-1}; UV λ_{max} (CH_2Cl_2) 256 (log ϵ 4.45), 286 (4.09), 381 nm (4.01). Anal. Calcd for $C_{18}H_{16}O_2Pd$: C, 58.32; H, 4.35. Found: C, 58.31; H, 4.29.

Bis(μ-chloro)bis(η^3-indenyl)palladium(II) (17). To a solution of sodium methoxide (0.128 g, 2.38 mmol) in dry methanol (20 mL) was added indene (0.15 mL, 1.3 mmol) and Li_2PdCl_4 (0.455 g, 2.07 mmol). After the solution was stirred for 4 h at room temperature, the resulting reddish brown precipitates were collected by filtration, washed with methanol and ether, and dried under reduced pressure to yield 0.279 g (84%) of **17**: mp (decomp) 155 °C; ^1H NMR (Me_2SO-d_6) δ 6.31 (2 H, d, J = 3 Hz, H-1,3), 6.99 (1 H, t, J = 3 Hz, H-2), 7.08 (center of AA'BB'); ^{13}C NMR (Me_2SO-d_6) δ 85.4 (C-1), 114.0 (C-2), 118.8 (C-5), 127.4 (C-4), and 136.9 (C-3a); IR (Nujol) 378, 422, 537, 588 cm^{-1}; UV λ_{max} (CH_2Cl_2) 277 (sh, log ϵ 4.75), 288 (4.84), 370 nm (3.86). Anal. Calcd for $C_{18}H_{14}Pd_2Cl_2$: C, 42.06; H, 2.75; Cl, 13.80. Found: C, 41.84; H, 2.78; Cl, 14.02.

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Appendix

Our calculations are of the extended Hückel type[20] with a weighted H_{ij} approximation. The Coulomb integrals and orbital exponents are listed in Table I. Orbital exponents of Pd 4d, 5s, and 5p are those given by Basch and Gray,[21] while the H_{ii}'s were taken from previous work.[22]

Geometrical assumptions included the following: phenalenyl and indenyl, C–C = 1.41 Å and C–H = 1.09 Å; Pd(acac), Pd–O = 2.1 Å and O–C = 1.23 Å, C–C = 1.52 Å, C–H = 1.09 Å, and C–C–C = 120°.

Registry No. 10, 73409-59-3; **14**, 203-80-5; **15**, 88582-21-2; **17**, 90624-27-4; **23**, 90624-28-5; Li_2PdCl_4, 15525-45-8; $PdCl_2$, 7647-10-1; Tl(acac), 14219-90-0; Pd, 7440-05-3; indene, 95-13-6.

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