metal faces as in $Fe_3(CO)_9(\mu_3\text{-}N_2CPh_2)_2$,[9] the multisite interaction in **2** has not previously been observed.

In an effort to generate a diphenylalkylidene ligand from the complexed Ph_2CN_2 molecule, complexes **2** were photolyzed in benzene, affording small amounts of **3**. Much higher yields (50–60%) were obtained by passing a stream of CO into **2** (200 mg) in toluene (25 mL) for 3.5 h. Crystals of **3** precipitated from concentrated solutions held at −20 °C. An X-ray analysis of **3** (R = *i*-Pr) revealed the structure shown in Figure 2.[10] The molecule is derived from **2** by insertion of a carbonyl group into the N(1)–N(2) bond and cleavage of a metal–metal bond by addition of an extra CO ligand. Thus the metal skeleton can be viewed as an Ru(1), Ru(2), Ru(4), Ru(5) butterfly with four strong Ru–Ru bonds and a long hinge edge (Ru(1)–Ru(5) = 3.3078 (7) Å), attached to a "spiked" atom Ru(3). The acetylide is bound to the Ru_4 butterfly fragment in a fashion reminiscent of the μ_4-vinylidene in $Ru_4(CO)_{10}(\mu_4\text{-}\eta^2\text{-}C{=}CH\text{-}i\text{-}Pr)(\mu_3\text{-}OH)(\mu\text{-}PPh_2)$[11] with C(14) interacting with all four metals. The terminal nitrogen atom N(1) of the new $NC(O)NCPh_2$ ligand caps the Ru(1), Ru(4), Ru(5) face with the carbonyl oxygen atom O(19) coordinated via a lone-pair interaction to Ru(3) (Ru(3)–O(19) = 2.142(4) Å). Bond distances within the urea-like ligand again emphasize a relationship to the nitrene form of a diazoalkane. The formation of an NC(O)N fragment in the conversion of **2** to **3** has an analogy in the synthesis of $Fe_2(CO)_6(PhNC(O)NPh)$ from phenylazide and $Fe_2(CO)_9$,[12] but the bonding mode in **3** is unique.

These results suggest that the availability of reaction pathways and coordination modes in higher nuclearity clusters which are not accessible in mono- or binuclear systems may present new opportunities to trap and examine the chemistry of unsaturated nitrogen species.

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Registry No. **1** (R = Ph), 883-40-9; **2** (R = Ph), 105121-70-8; $\mathbf{2}\cdot C_6H_6\cdot C_7H_8$ (R = Ph), 105121-72-0; **2** (R = *i*-Pr), 105139-45-5; **3** (R = Ph), 105121-71-9; **3** (R = *i*-Pr), 105121-73-1; $\mathbf{3}\cdot C_7H_{16}$ (R = *i*-Pr), 105121-74-2; **4** (R = Ph), 105121-69-5; **4** (R = *i*-Pr), 90696-73-4; Ru, 7440-18-8.

Supplementary Material Available: Table S1, additional data on intensity collection, structure solution and refinement for **2** and **3**, Tables S2 and S3, atomic positions (fractional × 10^4) for **2** and **3**, Tables S4 and S5, anisotropic thermal parameters (×10^3) for **2** and **3**, and Tables S6 and S7, bond lengths (Å) and angles (deg) (21 pages). Ordering information is given on any current masthead page. Structure factors ($|F_o|$) vs. ($|F_c|$) are available on request from the authors.

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(10) For **3** (R = *i*-Pr), $Ru_5PO_{14}N_2C_{44}H_{27}\cdot C_7H_{16}$: red crystals were obtained by layering a saturated toluene solution with heptane. A prism measuring 0.18 × 0.20 × 0.20 mm^3 was selected for X-ray crystallographic analysis. The cluster crystallized in the triclinic system, space group $P\bar{1}$ with a = 10.496 (1) Å, b = 13.899 (2) Å, c = 18.966 (2) Å, α = 88.81 (1)°, β = 77.80 (1)°, γ = 79.71 (1)°, V = 2660.3 (5) $Å^3$, Z = 2, and μ(Mo Kα) = 14.51 cm^{-1}. The measured and calculated densities were 1.79 and 1.80 g cm^{-3}, respectively. A total of 5740 independent reflections were measured of which 4509 had $I \geq 3\sigma(I)$ and were used in the structure solution. The structure was also solved by using the heavy-atom method. Hydrogen atoms were not located. Least-squares refinement of the atomic coordinates and anisotropic thermal parameters converged to R = 0.032 and R_w = 0.037. Additional information is given in Table S1.

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Competitive Metalation Reactions between Aliphatic and Aromatic Carbon Atoms in *N*-Benzylideneamines. X-ray Molecular Structure of $[\overline{\mathrm{Pd}\{1\text{-}CH_2\text{-}2\text{-}(HC{=}N}C_6H_5)\text{-}3,5\text{-}(CH_3)_2C_6H_2\}BrPPh_3]$

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Summary: $2,4,6\text{-}(CH_3)_3C_6H_2CH{=}N(CH_2)_nC_6H_5$ (n = 0, 1, or 2) react with $Pd(AcO)_2$ to give six-membered metallacycles possessing an aliphatic carbon–metal bond, in preference to four-, five-, or six-membered ring compounds with an aromatic carbon–metal bond.

The activation of aliphatic C–H bonds is a most important topic in organometallic chemistry. Cyclometalations are a way to reach the selective funtionalization of these bonds, but in some cases they can be a competitive process in the activation of alkanes.

The cyclometalation of N-donor ligands[1] shows a strong tendency to form five-membered rings; furthermore the aromatic carbons are activated more easily than the aliphatic carbons. To date, some cyclometalated complexes containing a six-membered ring and a metal–C(sp^2) bond have been described,[2] but few six-membered metallacycles containing an aliphatic carbon–metal bond have been obtained by cyclometalation. For example, Hiraki et al.[3a] have prepared $[\overline{\mathrm{Pd}(CH_2CMe_2CH_2C_5H_4N})(AcO)]_2$, from 2-neopentylpyridine and $Pd(AcO)_2$. Newkome et al. have recently obtained six- and seven-membered cyclometalated Pd(II) complexes, which contain pyridine, phenanthroline, or bipyridine moieties from the free ligands and $PdCl_2$, in the presence of K_2CO_3 to produce the abstraction of acidic hydrogens.[3b,c] The metalation of aromatic carbons is not possible in any case.

We herein report the cyclometalation of benzylideneamines $2,4,6\text{-}(CH_3)_3C_6H_2CH{=}N(CH_2)_nC_6H_5$ where, for the first time, the metalation of an aliphatic carbon with a six-membered ring takes place in preference to metalation of an aromatic carbon with a five-membered metallacycle.

Murahashi[4] obtained the five-membered compound by metalation of $2\text{-}(CH_3)C_6H_4CH{=}NC_6H_5$ and $Pd(AcO)_2$, even when the formation of a six-membered ring is possible by metalation of the ortho-methyl group. Rys et al.,[2f] when studying 1-[(2,6-dimethyl-4-hydroxyphenyl)azo]-2-

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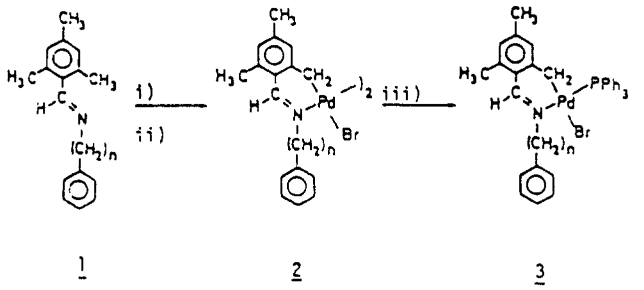
Scheme I[a]



[a] **a** (n = 0); **b** (n = 1); **c** (n = 2). (i) $Pd(AcO)_2$, $MeCO_2H$, reflux, 1 h and 30 min; (ii) LiBr, EtOH, reflux, 30 min; (iii) PPh_3, $(Me)_2CO$, reflux, 45 min.

methylnaphthalene, only accomplish metalation of the peri-carbon atom of the naphthyl group with formation of a six-membered ring, even when a five- or six-membered ring with Pd–C(sp^3) bonds would have resulted if the metalation had taken place at the methyl groups. These results illustrate the easier cleavage of aromatic C–H bonds as compared to aliphatic C–H bonds, as has been confirmed recently by Crabtree.[5]

The action of $Pd(AcO)_2$ on the amines 2,4,6-$(CH_3)_3C_6H_2CH{=}N(CH_2)_nC_6H_5$ (n = 0, 1, or 2) in anhydrous acetic acid has been examined (see Scheme I).

These imines permit a simultaneous comparison of the metalation tendency of the sp^3- or sp^2-carbon atoms and the importance of the number of members of the ring formed. Thus, metalation of the ortho-methyl groups gives six-membered rings, while the metalation of the ortho-phenyl carbons would give cyclometalated species with four-, five-, or six-membered rings, for n = 0, 1, or 2, respectively.

In the three cases, metalation of an ortho-methyl group with formation of a six-membered metallacycle takes place (ca. 70% yield). These results are specially remarkable for n = 1, since the metalation of the aromatic ortho carbon should yield a five-membered ring.

The novel cyclopalladated compounds **3** were unambiguously characterized by analytical and spectroscopic data.[6] The structure of **3a**[7] was confirmed by an X-ray crystallographic study.

The crystal structure of **3a** (Figure 1) consists of discrete molecules linked by van der Waals' forces. The Pd atom displays a distorted square-planar geometry but with usual bond lengths and angles around the metal. The bonding of C(21) and N(8) with the Pd atom causes the torsion of the C(1)–C(7) (31.8 (6)°) and N(8)–C(9) (−37.1 (6)°) bonds, which gives the C_4NPd six-membered ring, a half-skew-chair conformation with the Pd atom out of the plane (−1.325 Å).[8]

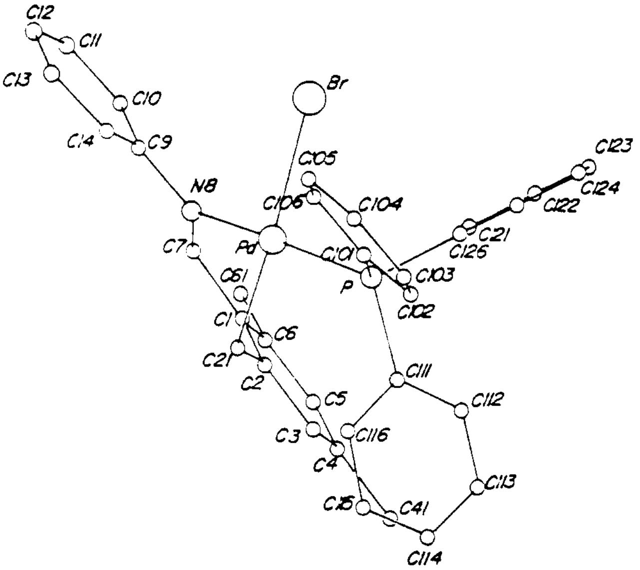


Figure 1. Molecular structure of **3a**. Important bond lengths (Å) and angles (deg): Pd–Br, 2.553 (1); Pd–N(8), 2.138 (4); Pd–C(21), 2.060 (5); Pd–P, 2.258 (1); C(21)–C(2), 1.483 (9); C(2)–C(1), 1.422 (8); C(1)–C(7), 1.460 (8); C(7)–N(8), 1.275 (8) Å; N(8)–Pd–Br, 90.8 (1); C(21)–Pd–N(8), 82.2 (2); P–Pd–Br, 93.1 (1); P–Pd–C(21), 93.9 (2); C(21)–Pd–Br, 172.9 (2); P–Pd–N(8) 169.6 (1); Pd–C(21)–C(2), 104.3 (4); C(21)–C(2)–C(1), 121.1 (5); C(2)–C(1)–C(7), 118.1 (5); C(1)–C(7)–N(8), 126.2 (5); C(7)–N(8)–Pd, 118.3 (4)°.

These results show that the original assumption, that metal ions preferring square-planar geometry favor five-membered ring, is unnecessarily limiting since a six-membered ring can also accommodate a central metal in a square-planar geometry as has been reported before.[3b,c]

Supplementary Material Available: Tables of anisotropic parameters, fractional coordinates, bond lengths, and bond angles (5 pages); a listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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(6) Complexes gave satisfactory elemental analyses. ^1H NMR in $CDCl_3$ (coupling constants in Hz): **3a**, δ 8.20 (d, $^4J_{P-H}$ = 12.7, 1 H, HC=N–), 7.77–7.24 (br, 20 H, PPh_3 and C_6H_5–), 6.66 (s, 1 H, ar), 5.60 (s, 1 H, ar), 2.87 (d, $^3J_{P-H}$ = 5.1, 2 H, CH_2Pd), 2.36 (s, 3 H, CH_3), 2.05 (s, 3 H, CH_3); **3b**, δ 8.18 (d, $^4J_{P-H}$ = 13.0, 1 H, HC=N–), 7.84–7.25 (br, 20 H, PPh_3 and C_6H_5–), 6.66 (s, 1 H, ar), 5.60 (br s, 3 H, CH_2N, and 1 H, ar), 2.35 (d, $^3J_{P-H}$ = 4.9, 2 H, CH_2Pd), 2.32 (s, 3 H, CH_3), 2.03 (s, 3 H, CH_3); **3c**, δ 7.92 (d, $^4J_{P-H}$ = 12.1, 1 H, HC=N–), 7.76–7.25 (br, 20 H, PPh_3 and C_6H_5–), 6.61 (s, 1 H, ar), 5.60 (s, 1 H, ar), 4.64 (br t, 2 H, NCH_2), 3.42 (t, 2 H, $C_6H_5CH_2$), 2.53 (d, $^3J_{P-H}$ = 5.4, 2 H, CH_2Pd), 2.24 (s, 3 H, CH_3), 2.03 (s, 3 H, CH_3).

(7) Crystal data: $C_{34}H_{29}NPBrPd$; M_r 668.9; monoclinic; a = 14.763 (2) Å, b = 19.525 (3) Å, c = 9.966 (1) Å; β = 90.81°; V = 2881 (1) Å^3, D_{calcd} = 1.54 g cm^{-3}; space group $P2_1/n$; Z = 4; $F(000)$ = 1104; λ(Mo Kα) = 0.71069 Å; μ(Mo Kα) = 21.82 cm^{-1}; room temperature; crystal dimensions 0.15 × 0.15 × 0.15 mm; Philips PW-1100 four-circle diffractometer; graphite-monochromatized Mo Kα radiation; ω–scan technique; scan width 1°; scan speed 0.03 deg s^{-1}; three reflections were measured every 2 h as orientation and intensity control; significant intensity decay was not observed; 4263 reflections in the range $2 < \theta < 25°$; 3850 observed [$I > 2.5\sigma(I)$]. The structure was solved by direct methods (MULTAN). The structure was refined by full-matrix square-planar method, using the SHELX76 computer program. The function minimized was $w|(F_o) - (F_c)|^2$, where $w = |\sigma^2(F_o) + 0.001(F_o)^2|^{-1}$. A total of 26 hydrogen atoms were obtained by a difference synthesis and refined with an overall isotropic temperature factor, while the remaining atoms were refined anisotropically. The final R was 0.041 (R_w = 0.044) for all observed reflections.

(8) The deviations from the mean plane are as follows: N(8), −0.168; C(7), 0.207; C(1), −0.042; C(2), −0.113; C(21), 0.116 Å.

Formates in Methanol Synthesis? The Reversible Production of Methyl Formate from Coordinated Formate

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Summary: The disproportionation of trimethylsilyl formate to methyl formate, carbon dioxide, and hexamethyldisiloxane is shown to be experimentally reversible and has been investigated in both the forward and reverse

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