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Nickel and Platinum 1,2-Dibromoacenaphthylene Chemistry

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Addition of 1,2-dibromoacenaphthylene to Ni(COD)$_2$/2L gives the oxidative-addition products *trans*-NiL$_2$(Br)(2-bromoacenaphthylen-1-yl) (L = PEt$_3$, PMe$_3$). The intermediate π-complex Ni(PMe$_3$)$_2$(η^2-1,2-dibromoacenaphthylene) is isolated at short reaction times for L = PMe$_3$. An analogous complex, Pt(PEt$_3$)$_2$(η^2-1,2-dibromoacenaphthylene), is formed in the reaction of Pt(PEt$_3$)$_4$ with 1,2-dibromoacenaphthylene and must be heated to induce oxidative-addition to *cis*-Pt(PEt$_3$)$_2$(Br)(2-bromoacenaphthylen-1-yl). Isomerization to the *trans* isomer is achieved by further heating. Reduction of *trans*-Ni(PEt$_3$)$_2$(Br)(2-bromoacenaphthylen-1-yl) with Na/Hg gives two different products depending on the workup. One procedure gives the Hg-bridged complex *trans,trans*-Ni(PEt$_3$)$_2$(Br)(acenaphthylen-1,2-diyl)Hg(acenaphthylen-1,2-diyl)Ni(PEt$_3$)$_2$(Br), while another procedure gives an unidentified complex that is also formed when the reduction is done with KC$_8$. Reduction of *trans*-Ni(PEt$_3$)$_2$(Br)(2-bromoacenaphthylen-1-yl) with Na/Hg in the presence of alkynes yields fluoranthenes, suggesting the formation of an acenaphthylyne complex, which couples with the alkynes. A small amount of *trans,trans*-Pt(PEt$_3$)$_2$(Br)(acenaphthylen-1,2-diyl)Hg(acenaphthylen-1,2-diyl)-Pt(PEt$_3$)$_2$(Br) is obtained from the reduction of *cis*-Pt(PEt$_3$)$_2$(Br)(2-bromoacenaphthylen-1-yl) with Na/Hg with *trans*-Pt(PEt$_3$)$_2$(Br)(2-bromoacenaphthylen-1-yl) as the major product. Reduction of *trans*-Pt(PEt$_3$)$_2$(Br)(2-bromoacenaphthylen-1-yl) with KC$_8$ results in debromination of the acenaphthylenyl ring.

Introduction

The ability of metals to stabilize reactive organic molecules by complexation is an early feature of organometallic chemistry.[1−4] Somewhat later, benzyne complex chemistry became particularly well developed, yielding complexes that retain considerable reactivity, allowing the synthesis of an extensive range of benzene derivatives.[5−12] Similar chemistry for polycyclic aromatic hydrocarbons has been much less explored and is restricted to naphthalyne complexes.[13,14] In an effort to expand this chemistry to other polycyclic aromatic hydrocarbons, we have investigated the synthesis of Ni and Pt acenaphthylyne[15,16] complexes using approaches analogous to those used to prepare Ni benzyne and naphthalyne complexes.[8,11−13] In the process we have examined the oxidative-addition chemistry of 1,2-dibromoacenaphthylene with Ni(0) and Pt(0) and discovered intermediate π-complexes. Although acenaphthylyne complexes were not isolated, trapping experiments suggest their transient presence for Ni.

Results

Addition of 1 equiv of solid 1,2-dibromoacenaphthylene to a mixture of Ni(COD)$_2$ and 2 equiv of PEt$_3$ in hexanes results in rapid formation of the oxidative-addition product *trans*-Ni(PEt$_3$)$_2$(Br)(2-bromoacenaphthylen-1-yl) (**1**) as an orange precipitate (Scheme 1). In contrast, a similar reaction in THF with PMe$_3$ in place of PEt$_3$ initially yields a mixture of two products, the PMe$_3$ analogue of **1** *trans*-Ni(PMe$_3$)$_2$(Br)(2-bromoacenaphthylen-1-yl) (**3**) and the π-complex Ni(PMe$_3$)$_2$(η^2-1,2-dibromoacenaphthylene) (**2**). A mixture of **2** and **3** is isolated at short reaction times. In solution at ambient temperatures the π-complex **2** converts to the oxidative-addition product *trans*-Ni(PMe$_3$)$_2$(Br)(2-bromoacenaphthylen-1-yl) (**3**) so that workup of the reaction after prolonged reaction times affords only **3**.

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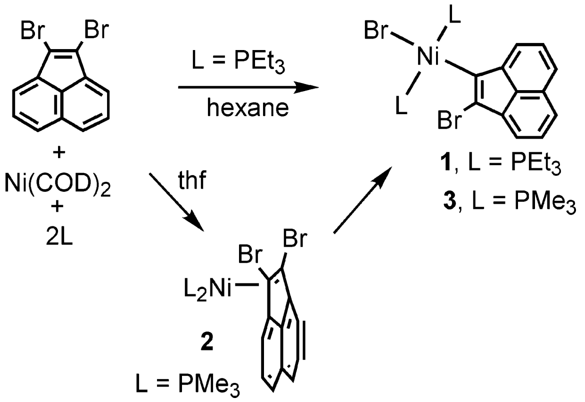
Scheme 1



NMR spectroscopic data on the compounds are characteristic of their structures. ^{31}P NMR spectra of **1** and **3** show a single resonance for the phosphine ligands in the region commonly observed for related oxidative-addition products.[17−19] ^{1}H NMR spectra show, in addition to the resonances for the phosphine ligands, six peaks (two overlapping) in the aromatic region consistent with the lack of equivalent protons on the acenaphthylenyl ligand. Signals for the 12 different carbons atoms of the acenaphthylenyl ligand are observed in the ^{13}C NMR spectra. Several of these show coupling to the phosphorus centers. The most downfield signals (~162 ppm) show the largest coupling (~40 Hz) and are assigned to the Ni-bonded carbon atom of the acenaphthylenyl ligand in **1** and **3**.

The ^{1}H spectrum of **2** (at −70 °C to prevent conversion to **3**) is simpler, consistent with the more symmetric structure of **2**, and shows a set of three peaks (two overlapping) in the aromatic region and a singlet for the PMe_3 ligands. The ^{13}C NMR spectrum in the aromatic region shows four strong signals assignable to the dibromoacenaphthylene ligand. Three weak signals are attributed to the remaining aromatic carbon atoms but could not be assigned with certainty due to the presence of small amounts of **3**. None of the peaks appear to show coupling to the phosphorus centers.

Complexes **1** and **2** were subjected to X-ray crystal structure analyses. An abbreviated summary of crystal data and data collection and processing is given in Table 1. Selected bond distances and angles are listed in Tables 2 and 3, and drawings for the complexes are given in Figures 1 and 2. Complex **3** was also subjected to an X-ray crystal structure analysis, but the quality of the structure was poor and the results serve mostly to confirm the identity of **3** (see Supporting Information). The structure of oxidative-addition product **1** is unexceptional and displays key metrical parameters (N−C, N−Br, Ni−P, etc.) similar to those of closely related complexes.[17−19] Complex **2**, however, is more unusual and must be compared to more distant relatives. The closest are the perfluoronaphthalene complex $(Et_3P)_2Ni(1,2\text{-}\eta^2\text{-}C_{10}F_8)$[20] and the arene complex $(^tBu_2PCH_2CH_2P^tBu_2)Ni(\eta^2\text{-}C_6F_6)$.[21] Of the two complexes the structure of the C_6F_6 complex most closely resembles that of **2** in terms of the metrical parameters surrounding the Ni-aromatic unit. The Ni−C distances of 1.954(4) and 1.934(4) Å for the C_6F_6 complex are similar to those for **2** (1.907(7) and 1.944(7) Å). The distances are in the same range but vary more for the naphthalene complex (1.959(4) and 1.899(4) Å). (A computational study attributes this variation to a soft potential energy surface for Ni−C bond length distortion.[20]) The Ni-bonded C−C distance for **2** lies between the values for the C_6F_6 complex (1.486(4) Å) and the naphthalene complex (1.438(6) Å) but considering the experimental error is indistinguishable from either complex. The bending back of the halogen atoms on the Ni-bonded carbon atoms, evaluated by the angle between the plane of the aromatic unit and the X−C−C−X plane (X = Br or F), is essentially the same at 45° for **2** and 44° for the C_6F_6 complex but significantly smaller for the naphthalene complex at 38°. Similarly, the carbon atoms of the aromatic unit of **2** and the C_6F_6 complex are coplanar (within less than 0.09 Å), and the angle between the aromatic unit plane and the Ni−C−C plane are very close at 114° for the C_6F_6 complex and 116° for **2**. On the other hand, the naphthalene ligand is less planar (0.2 Å out) and the angle between the naphthalene plane and the Ni−C−C plane is only 109°. Several Ni η^2-complexes of naphthalene and anthracene have been reported, but the Ni−aromatic interaction in these more electron-rich systems is evidently weaker with longer Ni−C bonds (1.96−2.01 Å), shorter C−C bonds (1.42 Å), and smaller angles between the aromatic unit plane and the Ni−C−C plane (101−105°).[22−24]

Platinum analogues of the nickel complexes are readily prepared but are more stable and give an intermediate *cis*-oxidative-addition product (Scheme 2). Thus, treatment of a hexane solution of $Pt(PEt_3)_4$ with 1,2-dibromoacenaphthylene gives a yellow precipitate of the π-complex $Pt(PEt_3)_2(\eta^2$-1,2-dibromoacenaphthylene) (**4**). NMR data are consistent with the mirror symmetry of **4**. A singlet with satellites (J_{PtP} = 3145 Hz) is observed at 8.75 ppm in the ^{31}P NMR spectrum. The ^{31}C NMR spectrum shows a peak at 148.75 ppm with satellites (J_{PtC} = 31.85 Hz), and this peak is assigned to the Pt-bonded C atoms of the 1,2-dibromoacenaphthylene.

Complex **4** is more stable than the nickel PMe_3 analogue (**2**) and converts only slowly in CH_2Cl_2 or with heating in toluene to the oxidative-addition product. In contrast to nickel, which directly gives the *trans* isomers **1** and **3**, the product is the *cis* isomer, *cis*-$Pt(PEt_3)_2$(Br)(2-bromoacenaphthylen-1-yl) (**5**). The ^{31}P NMR spectrum of **5** shows the expected pair of doublets (J_{PP} = 17.72 Hz), each with satellites. The downfield doublet satellites indicate a relatively small Pt−P coupling

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Table 1. Crystallographic and Data Collection Parameters for 1, 2, 4, 7 and 9[a]

	1	**2**	**4**	**7**	**9**
formula	$C_{24}H_{36}Br_2NiP_2$	$C_{18}H_{24}Br_2NiP_2$	$C_{24}H_{36}Br_2P_2Pt$	$C_{48}H_{72}Br_2HgNi_2P_4{\cdot}C_6H_6$	$C_{48}H_{72}Br_2HgP_4Pt_2{\cdot}2C_7H_8$
fw	605.00	520.84	741.38	1328.87	1707.79
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_12_12_1$	$P2_1$	$C2/m$	$C2/c$
a, Å	9.0730(6)	8.6824(16)	8.9778(5)	13.985(3)	29.7603(16)
b, Å	17.5804(11)	13.568(2)	15.5446(8)	13.971(3)	9.6127(5)
c, Å	16.3959(11)	17.428(3)	10.1242(5)	14.582(3)	23.9720(13)
α, deg	90	90	90	90	90
β, deg	92.174(1)	90	110.340(1)	95.790(3)	107.436(1)
γ, deg	90	90	90	90	90
V, Å^3	2613.4(3)	2053.0(6)	1324.80(12)	2834.7(11)	6542.7(6)
Z	4	4	2	2	4
d_{calc}, g/cm^3	1.54	1.68	1.86	1.56	1.73
μ, mm^{-1}	3.93	4.99	8.44	4.91	7.96
R1,[b] wR2[c]	0.0379, 0.0815	0.0550, 0.1111	0.0219, 0.0461	0.0718, 0.1695	0.0405, 0.0638

[a] λ, = 0.71070 Å (Mo), $T = -100$ °C. [b] $R1 = (\sum||F_o| - |F_c||)/\sum|F_o|$. [c] $wR2 = [(\sum w(F_o^2 - F_c^2)^2)/\sum w(F_c^2)^2]^{1/2}$.

Table 2. Selected Distances (Å) and Angles (deg) for *trans*-Ni(PEt$_3$)$_2$(Br)(1-bromoacenaphthylyn-1-yl), 1

Ni1−Br1	2.3591(5)	C1−C2	1.344(4)
Ni1−C1	1.874(3)	C1−C9	1.508(4)
Ni1−P2	2.2160(9)	C2−C10	1.480(4)
Ni1−P1	2.2238(9)		
P1−Ni1−P2	177.10(4)	C1−Ni1−Br1	174.52(10)
P1−Ni1−Br1	90.02(3)	C1−Ni1−P2	90.64(9)
P2−Ni1−Br1	90.43(3)	C1−Ni1−P1	89.19(9)

Table 3. Selected Distances (Å) and Angles (deg) for Ni(PMe$_3$)$_2$(η^2-1,2-dibromoacenaphthylene), 2, and Pt(PEt$_3$)$_2$(η^2-1,2-dibromoacenaphthylene), 4

	M = Ni (**2**)	M = Pt (**4**)
M1−C1	1.907(7)	2.078(4)
M1−C2	1.944(7)	2.075(4)
M1−P1	2.187(2)	2.2846(11)
M1−P2	2.192(2)	2.2887(11)
Br1−C1	1.944(7)	1.948(4)
Br2−C2	1.950(6)	1.942(4)
C1−C2	1.462(10)	1.485(6)
C1−C9	1.500(10)	1.482(6)
C2−C10	1.469(10)	1.483(6)
P1−M1−P2	104.79(9)	104.81(4)
C1−M1−P1	103.4(2)	105.44(12)
C2−M1−P2	106.8(2)	107.65(13)
C1−M1−P2	151.3(2)	149.46(12)
C2−M1−P1	147.8(2)	147.29(13)
C1−M1−C2	44.6(3)	41.92(17)
C2−C1−M1	69.0(4)	68.9(2)
C1−C2−M1	66.3(4)	69.1(2)
C9−C1−M1	117.9(5)	114.5(3)
C10−C2−M1	120.9(5)	115.1(3)
C2−C1−Br1	123.2(5)	121.5(3)
C1−C2−Br2	121.4(5)	121.7(3)
C9−C1−Br1	114.9(5)	114.9(3)
C10−C2−Br2	114.8(5)	115.2(3)
C2−C1−C9	106.4(6)	107.0(3)
C1−C2−C10	108.1(6)	106.6(4)
M1−C1−Br1	117.5(4)	121.6(2)
M1−C2−Br2	116.5(3)	120.7(2)

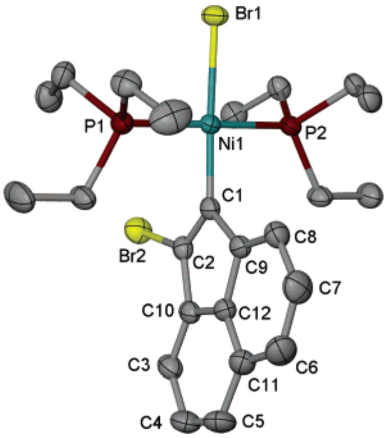


Figure 1. Drawing of *trans*-Ni(PEt$_3$)$_2$(Br)(1-bromoacenaphthlyn-1-yl) (**1**). Hydrogen atoms omitted here and in the following figures for clarity. Atoms are represented as 50% probability ellipsoids here and in following figures unless specified otherwise.

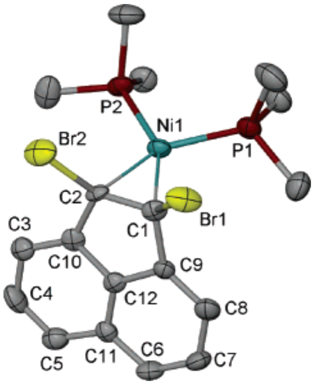
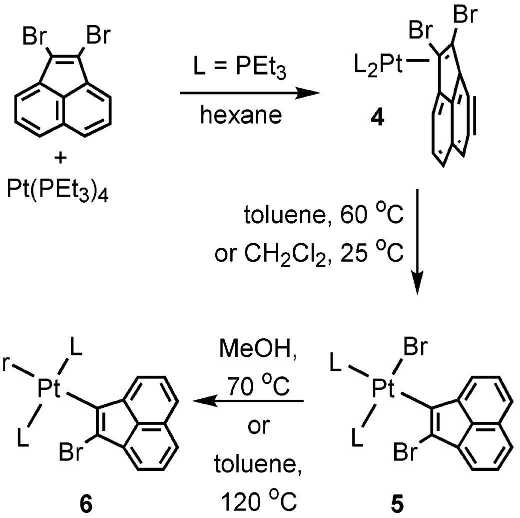


Figure 2. Ni(PMe$_3$)$_2$(η^2-1,2-dibromoacenaphthylene) (**2**).

(1835 Hz), indicating that the resonance should be assigned to the P atom *trans* to the strongly donating C atom of the bromoacenaphthylenyl ligand. The upfield doublet (4.92 ppm) with larger Pt−P coupling (3938 Hz) is assigned to the P atom *trans* to the weaker donating Br ligand. The ^{13}C NMR signal for the Pt-bonded carbon atom is found at 159.83 ppm as a doublet of doublets due to coupling to the *trans* and *cis* P atoms. Isomerization of **5** to the *trans*-isomer **6**, the analogue of **1** and **3**, is achieved by briefly refluxing **5** in MeOH or by prolonged refluxing in toluene. As a result of the isomerization and the increase in symmetry, the ^{31}P NMR phosphine signals simplify to a singlet with satellites. The ^{13}C signal for the Pt-bonded carbon atom also becomes a singlet with satellites as the carbon evidently loses coupling to the P atoms when both phosphines move into a *cis* position with respect to the carbon atom.

An X-ray crystal structure determination of **4** confirmed the structure. An abbreviated summary of crystal data and data collection and processing is given in Table 1. Selected bond distances and angles are listed

Scheme 2



in Table 3, and a drawing of the complex is given in Figure 3. Complex **5** was also subjected to an X-ray crystal structure analysis, but the structure is badly disordered (see Supporting Information). The structure of **4** is very similar to that of **2** but with the expected increase in the bond distances around the Pt center. The acenaphthylene metrical parameters are essentially identical, and as found for **2**, the carbon atoms of the acenaphthylene ligand are coplanar (within 0.03 Å). The bending back of the bromine atoms on the Pt-bonded carbon atoms, evaluated by the angle between the plane of the acenaphthylene moiety and the Br−C−C−Br plane, is slightly reduced for **4** (43°) from the analogous angle for **2** of 45°. More dramatic is a reduction in the angle between the acenaphthylene plane and the M−C−C plane, which is only 108° for **4** as compared to 116° for **2**.

As discussed above, the structure of the Ni complex **2** compares favorably with that of the Ni arene complex (^{t}Bu$_2$PCH$_2$CH$_2$P^{t}Bu$_2$)Ni(η^2-C$_6$F$_6$). An analogous platinum C_6F_6 complex is not available for comparison with **4**, but several CF$_3$-substituted η^2-arene complexes have been structurally characterized. Chemically, the most similar to **4** is $(Et_3P)_2Pt(\eta^2\text{-}C_6(CF_3)_6)$.[25] However, structurally this complex differs significantly from **4** in having a strongly disrupted nonplanar aromatic unit. Closer structural matches are found with the less substituted arene complex (^{t}Bu$_2$PCH$_2$P^{t}Bu$_2$)Pt(η^2-1,3,5-C$_6$H$_3$(CF$_3$)$_3$) and two related derivatives.[26] The coordinated arene ligands are planar, as is the acenaphthylene ligand in **4**, and the angles between the arene plane and the Pt−C−C plane are ~105°, close to the analogous value of 108° for **4**. The Pt−C distances in the arene complexes are slightly longer (average = 2.115(7) Å) as compared to those in **4** (2.078(4) and 2.075(4) Å), whereas the coordinated C−C distances are the same within experimental error (1.472(6), 1.472(7), and 1.453(13) Å for the arene complexes and 1.485(6) Å for **4**). Thus, as found for the Ni complex **2** (see above), the structure of **4** compares favorably with electron-deficient arene complexes as long as the arene is not highly substituted.

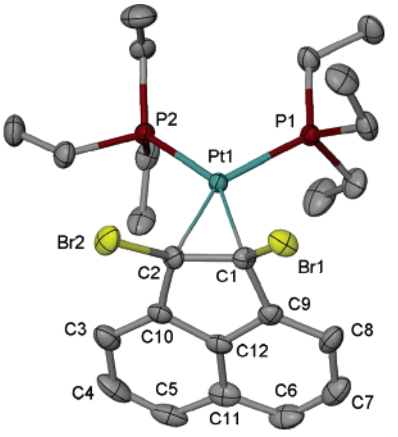
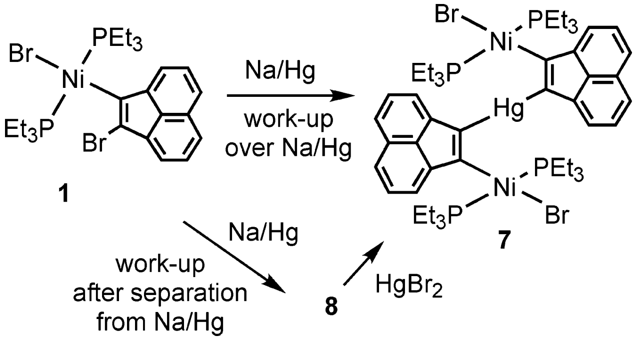


Figure 3. Drawing of the structure of Pt(PEt$_3$)$_2$(η^2-1,2-dibromoacenaphthylene) (**4**).

Scheme 3



Reduction Reactions. With the goal of preparing acenaphthylyne complexes analogous to known benzyne complexes[8,11,12,27,28] the Ni and Pt complexes prepared above were treated with reducing agents. Only the PEt$_3$ derivatives gave successful (identifiable major products) reduction reactions. Thus, stirring the Ni oxidative-addition complex **1** with excess 0.5% sodium amalgam in hexane gave a dark red solution. Examination of the solution by ^{31}P NMR spectroscopy revealed a new peak at 18 ppm. Removal of the volatiles from the reaction mixture (including the sodium amalgam) followed by extraction of the residue and amalgam with toluene gave a dark red toluene solution, but the ^{31}P NMR spectrum now showed a peak at 10 ppm. Concentration of the solution followed by cooling of the concentrate to −20 °C yielded deep red crystals, which proved by X-ray crystallography to be the Hg-bridged complex **7** (Scheme 3). A drawing of the structure is given in Figure 4. An abbreviated summary of crystal data and data collection and processing is given in Table 1, and selected bond distances and angles are listed in Table 4. The coordination environment of the Ni centers is essentially identical to that of the oxidative-addition product **1** (see above). Similarity is to be expected since the only change from **1** is the replacement of the ring bromine atom with an Hg atom. The only new feature that could result from this substitution would be the formation of a Ni−Hg dative bond. However, the Ni−Hg separation of 3.3881(19) Å is well beyond that observed (2.756(7) Å) in a complex thought to contain a Ni(II)−Hg(II) dative bond,[29] most likely indicating a negligible interaction.

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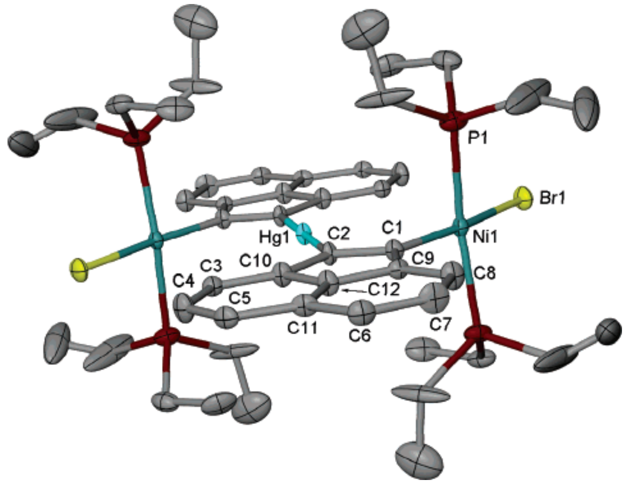


Figure 4. Drawing of the solid-state structure of **7**. Labeled and unlabeled atoms are related by an inversion center at the Hg atom position and a mirror in the metal-bromine-acenaphthylene plane (30% probability ellipsoids).

Table 4. Selected Distances (Å) and Angles (deg) for 7 and 9

	M = Ni (**7**)	M = Pt (**9**)
Hg1−C2	2.071(12)	2.057(5)
Hg1−M1	3.3881(19)	3.4594(3)
M1−C1	1.869(14)	2.004(6)
M1−-P1	2.211(4)	2.3035(16)
M1−-P2		2.3124(17)
M1−Br1	2.343(2)	2.5194(7)
C1−C2	1.337(19)	1.354(7)
C2−Hg1−C2	180.0(6)	180.00(19)
P1−M1−P2[a]	167.85(19)	176.45(6)
P1−M1−Br1	92.66(10)	89.90(5)
P2−M1−Br1		88.73(5)
C1−M1−P1	88.28(12)	90.97(16)
C1−M1−P2		90.50(16)
C1−M1−Br1	170.5(4)	178.04(17)
C2−C1−M1	120.3(10)	123.4(4)
C9−C1−M1	131.2(11)	127.7(4)
C2−C1−C9	108.6(12)	108.7(5)
C1−C2−Hg1	122.3(10)	119.1(4)
C10−C2−Hg1	127.2(10)	131.6(4)
C1−C2−C10	110.5(12)	109.2(5)

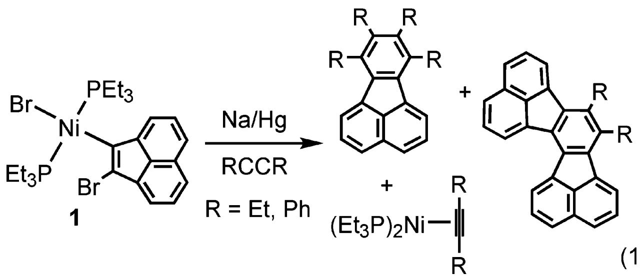
[a] P1−M−P1 for M = Ni.

NMR data are consistent with the solid-state structure. The ^{1}H NMR spectrum shows, in addition to the resonances for the phosphine ligands, six peaks (two overlapping) in the aromatic region for the six inequivalent protons of the acenaphthylendiyl ligand. The ^{13}C spectrum resembles that of parent **1** with a slight downfield shift of the Ni-bonded carbon signal from 161.71 to 169.69 ppm.

A different product **8**, apparently the precursor of **7**, is isolated from the reaction of **1** and sodium amalgam when the reaction solution is separated from the excess amalgam prior to removing the volatiles. Toluene extraction of the residue gives a red solution, which shows a peak at 18 ppm in its ^{31}P NMR spectrum. This is unchanged from that of the original reaction mixture, suggesting that workup in the presence of excess amalgam caused conversion of the original reduction product **8** to **7**. (The reaction of **8** with $HgBr_2$ gives **7** in low yield by NMR.) The ^{1}H NMR spectrum of **8** in the aromatic region shows two doublets and a doublet of doublets in a 1:1:1 ratio, consistent with a symmetric acenaphthylene moiety (2H, 2H, and 2H). The triethylphosphine ligand resonances appear as two multiplets (2:3 ratio) where integration indicates approximately two phosphine ligands for each acenaphthylene moiety. Also present is an overlapping doublet of triplets (J = 14.7 and 7.3 Hz) at −0.43 ppm. As we have not been successful at purification or crystallization of **8**, we are not certain if this signal is associated with the complex. However, this peak is also present when **8** is prepared by the reduction of **1** with KC_8, and it appears with about the same relative integration ratio (2H) in every sample. COSY experiments indicate that this peak is coupled to a multiplet partially buried under the PEt_3 methyl resonance and a weak septet (~0.5H) at 0.51 ppm.

The ^{13}C NMR spectrum of **8** contains numerous weak peaks consistent with the impure nature of **8**. The major signals in the aromatic region consist of five peaks: a triplet (J = 3.0 Hz) at 149.0 ppm and singlets at 132.44, 127.22, 121.87, and 120.26 ppm. A symmetric acenaphthylene moiety requires seven peaks in the aromatic region but with two representing single internal carbon atoms while the others represent two carbon atoms. Thus, two of the seven peaks are expected to be weak and are probably among the ~15 weak peaks in the aromatic region. The triethylphosphine peaks are found at 18.90 and 8.79 ppm. Curiously, the 18.90 ppm peak, attributed to the phosphine CH_2 group carbon atoms, appears to be a quintet (J = 5.1 Hz) instead of a triplet, as observed in **1** and **7**. In addition to the phosphine ligand peaks, three smaller but still strong singlets are observed at 31.91, 23.00, and 14.29 ppm.

The NMR spectral data may be interpreted as **8** being an acenaphthylyne complex but in combination with impurities. An acenaphthylyne complex should react with alkynes, like the analogous benzyne complexes, to give coupling products. Solutions of **8** are unchanged after alkyne addition, indicating that **8** is probably not an acenaphthylyne complex. The formation of **7** from **8** suggests that **8** is related to an acenaphthylyne complex and perhaps formed from an unstable acenaphthylyne complex. To explore this possibility, **1** was reduced with Na/Hg in the presence of alkynes (eq 1). The expected substituted fluoranthenes (35% yield for R = Et) from the coupling of two alkynes with acenaphthylyne were observed. Also formed were the substituted acenaphtho-[1,2-*j*]fluoranthenes (31% yield for R = Et), from the coupling of two acenaphthylynes and one alkyne, and the Ni alkyne complexes $(Et_3P)_2Ni(\eta^2\text{-}C_2R_2)$. A similar coupling of two benzyne ligands and an alkyne has been observed with a Ni benzyne complex.[30]



(1)

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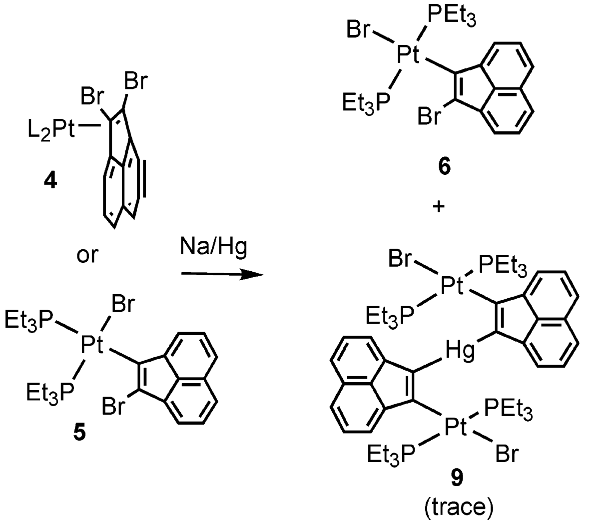
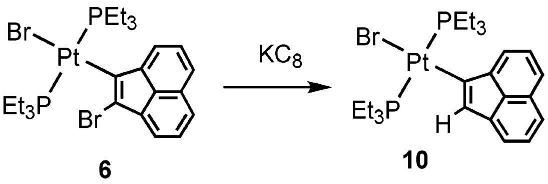
Reduction of the Pt complexes **4**, **5**, and **6** was investigated. Reduction of **4** or **5** with 0.5% Na/Hg in hexane or toluene gave after 12−24 h a green solution. However, NMR spectroscopy indicated that the solution contained **6** as the only major species. Reducing and cooling the solution yielded a few orange crystals shown by X-ray crystallography to be **9**, the Pt analogue of the Ni−Hg complex **7** (eq 2). Data for the structure determination of **9** are listed in Tables 1 and 4. Although the crystals are not isomorphous with those of the Ni analogue **7**, the complexes are isostructural and with the exception of the longer bonds involving the Pt center the metrical parameters are essentially the same. As in **7** the Pt−Hg distance of 3.4594(3) Å is much larger than those observed (2.51−2.83 Å) in complexes thought to contain a Pt(II)−Hg(II) dative bond,[29,31−35] indicating a negligible Pt−Hg interaction.



(2)

Complex **6** is inert to reduction by 0.5% Na/Hg, but KC_8 gives first a green solution, which turns dark red after 3 h. (Analogous aryl complexes are also difficult to reduce.[8]) Examination of the solution by ^{31}P NMR spectroscopy at first suggests that **6** remains (peak at 14 ppm); however, the Pt−P coupling constant of 2588 Hz, while similar to **6** (2661 Hz), is significantly different. A glassy red solid is isolated by removal of the volatiles, giving impure **10**, which could not be further purified and was characterized by solution NMR spectroscopy. ^1H and ^{13}C NMR spectra for **10** are also similar to **6**, suggesting a similar structure. One additional peak in the ^1H NMR spectrum of **10** is apparent and gives the final clue to the identity of **10**. The additional peak represents a single proton in the olefinic region and shows P−H coupling to two equivalent phosphine ligands and ^{195}Pt satellites. These observations strongly suggest that **10** is *trans*-[$Pt(PEt_3)_2(Br)$(1-acenaphthylenyl)], the debrominated analogue of **6** (eq 3). Complex **10** is also obtained from the KC_8 reduction of **5**.



Discussion

Oxidative-addition of organohalides to low-valent metal complexes is a classic method for the synthesis of organometallic complexes.[36,37] This method has been extensively applied to the preparation of Ni(II) and Pt(II) complexes from Ni(0) and Pt(0) starting materials, and with aryl halides the reactions generally proceed without the formation of intermediates.[38−40] We were therefore somewhat surprised to isolate the π-complexes **2** (Scheme 1) and **4** (Scheme 2) in the reactions with 1,2-dibromoacenaphthylene. The difference is the olefinic character of the 1,2-double bond of the acenaphthylene unit. Acenaphthylene itself shows this character and has yielded several π-complexes through coordination of the 1,2-double bond.[41−48] With this point of view, 1,2-dibromoacenaphthylene resembles more a vinyl halide than an aryl halide. Oxidative-addition of vinyl halides to group 10 metals has attracted attention due to the importance of group 10 metal catalyzed coupling reactions of vinyl halides.[49,50] Coordination of the vinyl halide through the C−C double bond is believed to be on the path to oxidative-addition, and Pd and Pt π-complexes that subsequently undergo oxidative-addition have been isolated or observed.[49,51−57] However,

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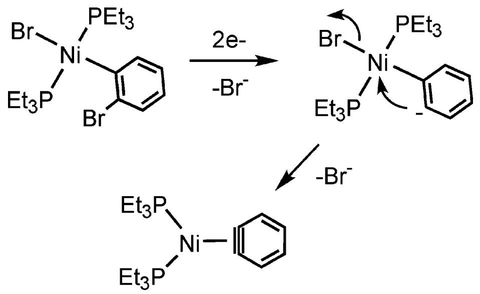
Scheme 4

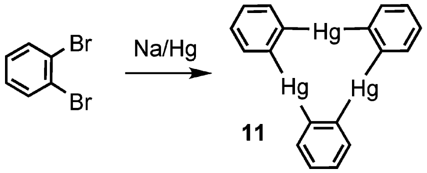


for Ni the only vinyl halide π-complexes to have been isolated are stable to oxidative-addition,[58−64] marking **2** a rare example of a Ni(0) π-complex that subsequently undergoes oxidative-addition.[20]

Oxidative-addition complexes **1**, **3**, **4**, and **6** and π-complexes **2** and **4** are potential precursors to acenaphthylyne complexes by reduction. Only for the Ni complexes does this appear to have been at least partially successful. Even then, trapping experiments with alkynes were required to find strong evidence for the formation of an acenaphthylyne complex (eq 1). The isolated cycloaddition products and the alkyne complexes $(Et_3P)_2$-Ni(η^2-RCCR) (see eq 1) are what would be expected from a reactive acenaphthylyne and are analogous to products obtained from alkyne reactions of Ni benzyne complexes.[30] When alkynes are not used to trap the acenaphthylyne complex, impure and incompletely characterized reduction product **8** is obtained. Although the spectroscopic data for **8** and its apparent conversion to the Hg-bridged complex **7** are not inconsistent with an acenaphthylyne complex, its lack of reactivity with alkynes indicates that it is not an acenaphthylyne complex. Complex **8** is presumably a rearrangement or decomposition product of the reactive acenaphthylyne complex.

That acenaphthylyne complexes would be difficult to obtain and unstable is not unexpected. Acenaphthylyne is considerably more strained than benzyne, suggesting a lower stability and greater reactivity for its complexes.[15,16] Difficulties in the formation of an acenaphthylyne complex are suggested by the mechanism favored by Bennett for Ni benzyne complex formation (Scheme 4).[8] In this mechanism the Ni-bound bromoaryl group is converted into an aryl anion, which then attacks the metal center. The smaller internal angles in the five-membered ring of an acenaphthylene complex make the geometry of such an attack less favorable. A similar problem has been encountered in the synthesis of a cyclopentyne complex.[65] The debromination of Pt acenaphthylene complex **6** to **10** upon reduction may occur through adventitious protonation of the anion before attack at the Pt center can occur. Alternatively, debromination may occur through a radical process.

The isolation of the Hg-bridged complexes **7** and **9** is curious. The formation of organomercurials from the reaction of organohalides with Na/Hg is known. An example is the synthesis of 1,2-phenylene mercury trimer **11** from 1,2-dihalobenzenes and Na/Hg (eq 4).[66] Presumably an analogous process is involved in the formation of the mercury-bridged complexes **7** and **9**. However, the low conversion of the Pt complex and the apparent formation of **7** when solutions of **8** are evaporated in the presence of excess Na/Hg are difficult to understand. Our inability to identify **8** further hampers our understanding of the formation of **7**.



(4)

Conclusions

Reaction of 1,2-dibromoacenaphthylene with $Ni(COD)_2$/2L (L = PMe_3, PEt_3) and $Pt(PEt_3)_4$ gives oxidative-addition products. For Pt and for Ni with L = PMe_3, isolated π-complexes precede the oxidative-addition products. Reduction of the oxidative-addition complexes does not give isolable acenaphthylyne complexes but rather debromination of the coordinated 2-bromoacenaphthylene ring for Pt and an identified complex for Ni, which incorporates Hg on workup in the presence of excess Na/Hg to give a mercury-bridged dimer. Trapping experiments with alkynes suggest that an unstable acenaphthylyne complex is formed in the reduction of the Ni oxidative-addition products. The failure to isolate acenaphthylyne complexes is attributed to the large strain associated with a five-membered acenaphthylyne ring.

Experimental Section

General Procedures. Experiments were performed under a dinitrogen atmosphere in a Vacuum Atmospheres Corporation drybox or on a Schlenk line. Solvents were dried by standard techniques and stored under dinitrogen over 4 Å molecular sieves or sodium metal. $Pt(PEt_3)_4$[67] and 1,2-dibromoacenaphthylene[68] were synthesized by literature procedures. Phosphines and $Ni(COD)_2$ were purchased from commercial sources (Strem or Aldrich Chemicals) and were used as received. NMR spectra were recorded on a Bruker AMX-250, -300, or -500 spectrometer at ambient probe temperatures. Shifts are given in ppm with positive values downfield of TMS (^1H and ^{13}C) or external H_3PO_4 (^{31}P). ^{13}C and ^{31}P NMR spectra were recorded in proton-decoupled mode. Desert Analytics, Atlantic Micro Lab, or National Chemical Consulting performed the microanalyses (inert atmosphere). The presence of solvents of crystallization in the analyzed samples was

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confirmed by NMR spectroscopy. The Chemistry Mass Spectrometry Facility at the Ohio State University collected the mass spectral data for the organic products.

Synthesis of Ni(PEt$_3$)$_2$(Br)(C$_{12}$H$_6$Br) (1). Ni(COD)$_2$ (275 mg, 1.00 mmol) was placed in a vial, and 2.95 g of a 10% PEt$_3$ (295 mg, 2.50 mmol) in hexane was added with stirring. The yellow solid dissolved to give an orange solution. After 5 min, orange solid 1,2-dibromoacenaphthylene (310 mg, 1.00 mmol) was slowly added in portions with stirring. The solid dissolved and the solution darkened and then deposited the orange product. The mixture was placed in a freezer at −20 °C for 1 h. The solution was then decanted off the orange solid product, which was washed with cold hexane and dried in vacuo. Yield: 485 mg (80%). Crystals for X-ray analysis were grown from toluene/hexane.

^{1}H NMR (250 MHz, C$_6$D$_6$): 8.21 (d, J = 6.74 Hz, 1H), 7.52 (d, J = 8.16 Hz, 1H), 7.33 (m, 4H), 1.55 (dm, J = 54.36 Hz, 12H), 1.01 (quin, $J_{HH} \approx J_{PH}$ = 7.7 Hz, 18H, $\mathrm{CH_2C}H_3$). ^{13}C NMR (62.89 MHz, C$_6$D$_6$): 161.71 (t, J = 37.70 Hz), 145.43 (s), 141.69 (t, J = 3.97 Hz), 131.07 (s), 127.83 (s), 127.40 (s), 126.69 (s), 125.31 (s), 123.97 (s), 122.86 (t, J = 8.12 Hz), 116.34 (s), 15.39 (t, J = 12.98 Hz, $C\mathrm{H_2CH_3}$), 8.71 (s, $\mathrm{CH_2}C\mathrm{H_3}$). ^{31}P NMR (101.25 MHz, C$_6$D$_6$): 13.0 (s). Anal. Calcd for C$_{24}$H$_{36}$Br$_2$NiP$_2$: C 47.65, H 6.00. Found: C 47.70, H 6.08.

Synthesis of Ni(PMe$_3$)$_2$(η^2-C$_{12}$H$_6$Br$_2$) (2) and Ni(PMe$_3$)$_2$(Br)(C$_{12}$H$_6$Br) (3). Trimethylphosphine (0.62 mL of a 1.0 M solution in THF) was added dropwise to a stirred THF solution (5 mL) of Ni(COD)$_2$ (68.9 mg, 0.25 mmol). After 5 min, solid 1,2-dibromoacenaphthylene (77.5 mg, 0.25 mmol) was slowly added to the orange stirred solution. The mixture became deep orange. If stirring is stopped shortly after the addition of the 1,2-dibromoacenaphthylene and hexane is slowly added, both rod-like crystals of the π-complex (**2**) and block-shaped crystals of the oxidative-addition complex (**3**) form at −20 °C. On the other hand, if the reaction mixture is stirred overnight at room temperature, only oxidative-addition complex (**3**) is obtained. In both cases, the deep orange products were isolated by decanting off the mother liquor, washing the crystals with hexane, followed by drying in vacuo. Yield: 80.0 mg (61%). Both **2** and **3** were characterized by X-ray crystallography. The π-complex (**2**) is not stable in solution at room temperature and readily converts into the oxidative-addition product (**3**). The NMR spectra of **2** were therefore obtained at low temperature and always show some **3**.

Data for **2**: ^{1}H NMR (250 MHz, CD$_2$Cl$_2$, −70 °C): 7.39 (d, J = 6.96 Hz, 2H), 7.27 (m, 4H), 1.18 (t, J = 3.93 Hz, 18H). ^{13}C NMR (62.89 MHz, CD$_2$Cl$_2$, −70 °C): 145.97 (s), 127.95 (s), 120.6 (s), 117.32 (s), 14.75 (t, J_{PC} = 12.4 Hz). (Weak peaks observed at 130.38, 128.92, and 126.05 are tentatively assigned to the remaining aromatic carbon atoms.) ^{31}P NMR (101.25 MHz, CD$_2$Cl$_2$, −70 °C): −16.1 (s). Samples are always contaminated with **3**, preventing meaningful elemental analysis.

Data for **3**: ^{1}H NMR (250 MHz, CD$_2$Cl$_2$): 7.91 (d, J = 6.68 Hz, 1H), 7.69 (d, J = 8.16 Hz, 1H), 7.52 (m, 2H), 7.40 (m, 1H), 7.16 (d, J = 6.65 Hz, 1H), 1.19 (t, J = 3.9 Hz, 18H). ^{13}C NMR (62.89 MHz, CD$_2$Cl$_2$): 162.29 (t, J_{PC} = 40.6 Hz) 144.68 (s), 141.11 (t, J_{PC} = 4.2 Hz), 130.62 (s), 128.12 (s), 127.67 (s), 127.15 (s), 126.66 (s), 124.77 (s), 123.90 (s), 122.0 (t, J_{PC} = 9.3 Hz), 116.34 (t, J_{PC} = 2.0 Hz), 14.44 (t, J_{PC} = 14.8 Hz). ^{31}P NMR (101.25 MHz, CD$_2$Cl$_2$): −11.6 (s). Anal. Calcd for C$_{18}$H$_{24}$Br$_2$NiP$_2$: C 41.51, H 4.64. Found: C 41.89, H 4.36.

Synthesis of Pt(PEt$_3$)$_2$(η^2-C$_{12}$H$_6$Br$_2$) (4). To a stirred hexane solution (5 mL) of Pt(PEt$_3$)$_4$ (250 mg, 0.3744 mmol) was added dropwise a hexane solution (10 mL) of 1,2-dibromoacenaphthylene (116.5 mg, 0.3758 mmol). The mixture was stirred for 2 h to give **4** as a yellow powder. The solvent was removed by decantation and the solid product washed with cold hexane (2 × 3 mL) and dried in vacuo. Yield: 240.0 mg (86%). Single crystals suitable for the X-ray analysis were grown from a concentrated toluene solution at room temperature.

^{1}H NMR (250 MHz, C$_6$D$_6$): 7.48−7.46 (m, 2H), 7.31−7.15 (m, 4H, partly overlapping with $\mathrm{C_6D_5}H$), 1.61−1.39 (m, 12H, $\mathrm{C}H_2\mathrm{CH_3}$), 0.77−0.55 (m, 18H, $\mathrm{CH_2C}H_3$). ^{13}C NMR (62.89 MHz, C$_6$D$_6$): 148.75 (s with satellites, J_{PtC} = 31.85 Hz), 122.36 (t, J_{PC} = 1.74 Hz), 118.79 (t, J_{PC} = 2.26 Hz), 17.42 (m, $C\mathrm{H_2CH_3}$), 8.07 (t, J_{PC} = 6.64 Hz, $\mathrm{CH_2}C\mathrm{H_3}$). (Remaining peaks are presumably buried under the C$_6$D$_6$ peak.) ^{31}P NMR (101.25 MHz, C$_6$D$_6$): 8.75 (s with satellites, $^1J_{PtP}$ = 3145 Hz). Anal. Calcd for C$_{24}$H$_{36}$Br$_2$P$_2$Pt: C 38.88, H 4.88. Found: C 38.60, H 4.69.

Synthesis of *cis*-[Pt(PEt$_3$)$_2$(Br)(C$_{12}$H$_6$Br) (5). Complex **4** (50.0 mg, 0.0674 mmol) dissolved in ~5 mL of toluene was heated for 6 h at 60 °C. A ^{31}P NMR spectrum showed the complete disappearance of **4** and the appearance of two doublets with satellites. The product was isolated as a yellow crystalline solid by reducing the volume and adding hexane. Yield: 48 mg (96%). Later it was found that **4** in CD$_2$Cl$_2$ readily converts to **5** without heating. Single crystals suitable for the X-ray analysis were grown from a concentrated toluene solution at −30 °C.

^{1}H NMR (500 MHz, CD$_2$Cl$_2$): 7.64−7.57 (m, 3H), 7.46−7.43 (m, 2H), 7.28 (d, J = 6.75 Hz), 1H), 2.16−2.10 (m, 6H, $\mathrm{C}H_2\mathrm{CH_3}$), 1.95−1.70 (dm, J = 85.15 Hz, 6H, $\mathrm{C}H_2\mathrm{CH_3}$), 1.28−1.07 (dm, J = 66.29 Hz, 18H, $\mathrm{CH_2C}H_3$). ^{13}C NMR (75.47 MHz, CD$_2$Cl$_2$): 159.83 (dd, J_{PC} = 114.71 Hz, 9.96 Hz), 147.55 (d with satellites, J_{PC} = 3.32 Hz, J_{PtC} = 24.53 Hz), 142.57 (d with satellites, J_{PC} = 7.39 Hz, J_{PtC} = 49.05 Hz), 130.15 (d, J_{PC} = 5.66 Hz), 127.72 (s), 127.40 (s), 127.37 (s), 125.81 (s), 125.58 (s with satellites, J_{PtC} = 24.45 Hz), 124.82 (s), 121.20 (d, J_{PC} = 2.72 Hz), 118.31 (s), 17.69 (dd with satellites, J_{PC} = 38.49 Hz, 2.40 Hz, J_{PtC} = 52.35 Hz), 15.64 (d with satellites, J_{PC} = 29.39 Hz, J_{PtC} = 20.57 Hz), 8.64 (d with satellites, J_{PC} = 2.29 Hz, J_{PtC} = 33.2 Hz), 8.47 (s with satellites, J_{PtC} = 16.51 Hz). ^{31}P NMR (101.25 MHz, CD$_2$Cl$_2$): 8.94 (d with satellites, J_{pp} = 17.72 Hz, $^1J_{PtP}$ = 1835 Hz, P *trans* to C), 4.92 (d with satellites, J_{pp} = 17.72 Hz, $^1J_{PtP}$ = 3938 Hz, P *trans* to Br).

Synthesis of *trans*-[Pt(PEt$_3$)$_2$(Br)(C$_{12}$H$_6$Br)] (6). Complex **4** (62.0 mg, 0.0836 mmol) was dissolved in 10 mL of methanol and heated for 7 h at 80 °C in a sealed flask. The color of the solution changed from yellow to light orange, and complex **6** was formed through the conversion of **4** to **5**, finally giving a singlet at 14 ppm in the ^{31}P NMR spectrum of the reaction mixture. Concentration of the methanol solution afforded orange microcrystals of **6**. Yield: 58.0 mg (94%). Complex **6** can also be prepared by heating a toluene solution of **4** or **5** at 120 °C for more than 24 h. Single crystals for X-ray analysis were grown from a toluene/hexane mixture at −30 °C.

^{1}H NMR (500 MHz, CD$_2$Cl$_2$): 7.66−7.56 (m, 3H), 7.46−7.40 (m, 2H), 7.29 (d, J = 6.39 Hz, 1H), 1.90−1.73 (dm, J_{PH} = 81.43 Hz, 12H, $\mathrm{C}H_2\mathrm{CH_3}$), 1.09−1.05 (m, 18H, $\mathrm{CH_2C}H_3$). ^{13}C NMR (75.47 MHz, CD$_2$Cl$_2$): 146.39 (s with satellites, J_{PtC} = 46.26 Hz), 145.37 (t, J_{PC} = 10.57 Hz), 142.50 (t with satellites, J_{PC} not resolved, J_{PtC} = 73.43 Hz), 130.76 (s), 127.76 (s), 127.62 (s), 127.44 (s), 126.46 (s), 125.51 (s with satellites, J_{PtC} = 36.38 Hz), 124.65 (s), 119.87 (t, J_{PC} = 5.1 Hz), 118.13 (s), 14.71 (m, $C\mathrm{H_2CH_3}$), 8.39 (m, $\mathrm{CH_2}C\mathrm{H_3}$). ^{31}P NMR (101.25 MHz, CD$_2$Cl$_2$): 14.1 (s with satellites, $^1J_{PtP}$ = 2588 Hz). Anal. Calcd for C$_{24}$H$_{36}$Br$_2$P$_2$Pt: C 38.88, H 4.88. Found: C 38.52, H 4.63.

Synthesis of [Ni(PEt$_3$)$_2$Br(C$_{12}$H$_6$)]$_2$Hg (7). Complex **1** (40 mg, 0.066 mmol) was suspended in 10 mL of hexane and stirred over excess 0.5% Na/Hg for 18 h. The orange mixture turned deep red. The ^{31}P NMR spectrum of the reaction solution showed a singlet at 18 ppm. The volatiles were removed in vacuo from the reaction mixture without separation from the excess Na/Hg. The residue was extracted with toluene and filtered through diatomaceous earth. (A ^{31}P NMR spectrum of the filtered extract showed a peak at 10 ppm as the only major peak.) Concentration of the filtrate to about 3 mL followed by cooling to −20 °C gave the deep red crystalline product **4**, which was isolated by decantation, washed with cold hexane, and dried in vacuo. Yield: 8.76 mg (21%). Single crystals suitable for X-ray were grown from a concentrated C_6D_6 solution of the complex.

^{1}H NMR (250 MHz, C_6D_6): 8.56 (d, J = 6.67 Hz, 1H), 8.06 (d, J = 6.61 Hz, 1H), 7.59 (m, 2H), 7.49 (t, J = 7.29 Hz, 1H), 7.33 (d, J = 8.18 Hz, 1H), 1.65 (dm, J = 26.4 Hz, 12H), 1.05 (m, 18H). ^{13}C NMR (62.89 MHz, C_6D_6): 169.69 (s, Hg-C), 148.71 (s), 146.50 (s), 133.27 (s), 128.83 (s), 128.68 (s), 127.34 (s), 127.00 (s), 124.27 (s), 122.95 (s), 120.11 (s), 15.61 (t, J = 12.6 Hz, $\mathit{C}H_2CH_3$), 8.82 (s, $CH_2\mathit{C}H_3$). (The Ni-C triplet expected at ~160 ppm may be too weak to observe.) ^{31}P NMR (101.25 MHz, CD_2Cl_2): 10.0 (s). Anal. Calcd for $C_{48}H_{72}Br_2HgNi_2P_4$: C 46.09, H 5.80. Found: C 46.25, H 5.73.

Formation of 8. The procedure was identical to that for **7** except the reaction mixture solution was decanted off of the excess Na/Hg before the volatiles were removed in vacuo. Extraction of the residue with toluene gave a deep red solution. A ^{31}P NMR spectrum of the solution showed a peak at 18 ppm as the only major peak, unchanged from that of the original reaction mixture. Repeated attempts to purify this major phosphorus-containing product (**8**) failed. Other reducing agents (Li, Na, Mg, KC_8) either failed to give **8** or gave **8** in a mixture of several major phosphorus-containing products.

^{1}H NMR (250 MHz, C_6D_6): 7.68 (d, J = 7.99 Hz, 2H), 7.51 (d, J = 7.93 Hz, 2H), 7.38 (m, 2H), 1.69−1.48 (m, 24H), 0.93 (m, 36H), 0.78 (apparent t, J = 7.6 Hz, ~1H), 0.51 (sept, J = 6.5 Hz, ~0.5H), −0.05 (overlapping dt, J = 14.2, 7.3 Hz, 2H). ^{13}C NMR (62.89 MHz, C_6D_6): 149.07 (t, J = 3.01 Hz), 132.44 (s), 127.22 (s), 123.09 (s), 121.87 (s), 120.26 (s), 18.89 (m, $\mathit{C}H_2CH_3$), 8.79 (s, $CH_2\mathit{C}H_3$). ^{31}P NMR (101.25 MHz, C_6D_6): 18.0 (s).

Reduction of 1 in the Presence of RCCR (R = Et, Ph). Excess (~20-fold) alkyne was added to a hexane solution (5 mL) of **1** (30.4 mg, 0.0502 mmol) followed by excess 0.5% Na/Hg. The reaction mixture was stirred for 15 h, after which time ^{31}P NMR spectroscopy showed a singlet at 27.0 (R = Et) or 21.0 (R = Ph) ppm for $(Et_3P)_2Ni(\eta^2\text{-RCCR})$. The solution was decanted from the Na/Hg, filtered, and evaporated to dryness. The residue was dissolved in 2 mL of THF. Aqueous HCl was added and the mixture extracted with Et_2O. The extract was dried with $MgSO_4$, and the organic compounds were separated on a silica gel column with hexane as eluent, giving (R = Et) 7,8,9,10-tetraethylfluoranthene (5.5 mg, 35%) and 4,5-diethylacenaphtho[1,2-*j*]fluoranthene (6.0 mg, 31%). For R = Ph, only impure 4,5-diphenylacenaphtho[1,2-*j*]fluoranthene could be isolated.

Data for 7,8,9,10-tetraethylfluoranthene: ^{1}H NMR (250 MHz, $CDCl_3$): 7.99 (d, J = 7.06 Hz, 1H), 7.77 (d, J = 8.16 Hz, 1H), 7.60 (dd, J = 7.19 Hz, 1H), 3.19 (q, J = 7.53 Hz, 2H, $C\mathit{H_2}CH_3$), 2.82 (q, J = 7.50 Hz, 2H, $C\mathit{H_2}CH_3$), 1.42 (t, J = 7.53 Hz, 3H, $CH_2C\mathit{H_3}$), 1.28 (t, J = 7.49 Hz, 3H, $CH_2C\mathit{H_3}$). ^{13}C NMR (75.47 MHz, $CDCl_3$): 139.99 (s), 137.61 (s), 137.25 (s), 135.49 (s), 133.17 (s), 129.88 (s), 127.73 (s), 125.75 (s), 122.51 (s), 22.93 (s), 21.94 (s), 15.96 (s), 14.13 (s). HRMS (electrospray): calcd for $[C_{24}H_{26}]^{+\bullet}$ 314.2029; found 314.2039. See the Supporting Information for the X-ray crystal structure.

Data for 4,5-diethylacenaphtho[1,2-*j*]fluoranthene: ^{1}H NMR (250 MHz, $CDCl_3$): 8.73 (d, J = 7.09 Hz, 1H), 8.15 (d, J = 7.17 Hz, 1H), 7.90 (t, J = 8.00 Hz, 2H), 7.81−7.67 (m, 2H), 3.39 (q, J = 7.50 Hz, 2H, $C\mathit{H_2}CH_3$), 1.53 (t, J = 7.49 Hz, 3H, $CH_2C\mathit{H_3}$). ^{13}C NMR (75.47 MHz, $CDCl_3$): 138.94 (s), 137.67 (s), 137.26 (s), 133.94 (s), 130.15 (s), 128.05 (s), 127.64 (s), 126.65 (s), 126.27 (s), 123.20 (s), 123.07 (s), 22.26 (s), 14.12 (s). HRMS (electrospray): calcd for $[C_{30}H_{22}]^{+\bullet}$ 382.1716; found 382.1685.

Data for 7,8,9,10-tetraphenylfluoranthene:[69] ^{1}H NMR (250 MHz, $CDCl_3$): 7.71 (d, J = 8.2 Hz, 2H), 7.31−7.29 (m, 12H), 6.90−6.84 (m, 12H), 6.61 (d, J = 7.04 Hz). ^{13}C NMR (75.47 MHz, $CDCl_3$): 131.40 (s), 131.28 (s), 130.07 (s), 128.14 (s), 126.59 (s). HRMS (electrospray): calcd for $[C_{40}H_{26}]^{+\bullet}$ 506.2029; found 506.2022.

Data for 4,5-diphenylacenaphtho[1,2-*j*]fluoranthene:[70] ^{1}H NMR (250 MHz, $CDCl_3$): 8.80 (d, J = 7.0 Hz, 2H), 7.94−7.75 (m, 4H), 6.47 (d, J = 7.15 Hz, 1H). ^{13}C NMR (75.47 MHz, $CDCl_3$): 140.62 (s), 139.85 (s), 139.81 (s), 139.24 (s), 137.15 (s), 136.46 (s), 129.59 (s), 128.29 (s), 127.88 (s), 127.71 (s), 127.61 (s), 127.06 (s), 126.87 (s), 126.49 (s), 126.42 (s), 125.39 (s), 123.91 (s), 123.16 (s), 123.04 (s). HRMS (electrospray): calcd for $[C_{38}H_{22}]^{+\bullet}$ 478.1716; found 478.1694.

Reaction of 4 or 5 with Na/Hg. Isolation of [Pt(PEt$_3$)$_2$Br(C$_{12}$H$_6$)]$_2$Hg (9). Complex **4** or **5** was stirred with excess 0.5% Na/Hg in hexane or toluene. After 12−24 h stirring a green solution was obtained that showed a singlet at ~14.0 ppm ($^1J_{PtP} \approx 2588$ Hz) by ^{31}P NMR spectroscopy. The solution was decanted from the Na/Hg, filtered, and after concentration kept at −30 °C to afford a few orange crystals. These were shown to be **9**, the Pt analogue of **8**, by an X-ray analysis. Insufficient material was isolated for NMR or elemental analysis.

Reaction of 6 with C$_8$K. Complex **6** (38.0 mg, 0.0513 mmol) was treated with 4 equiv of C_8K (28.0 mg, 0.2071 mmol) in toluene. After stirring for 3 h the orange solution had turned green and then deep red. A ^{31}P NMR spectrum of the solution showed a peak at the same chemical shift as **6** (14 ppm) but with a J_{PtP} of 2661 Hz instead of 2588 Hz. The solution was filtered and evaporated to dryness to give 30.0 mg of a glassy red solid (**10**). Attempts to purify or crystallize the solid were unsuccessful.

Data for the red product: ^{1}H NMR (500 MHz, CD_2Cl_2): 7.65 (d, J = 8.07 Hz, 1H), 7.60 (d, J = 6.59 Hz, 1H), 7.49−7.44 (m, 2H), 7.37−7.34 (m, 1H), 7.29 (d, J = 6.69 Hz, 1H), 6.58 (t, J = 1.76 Hz, $^1J_{PtP}$ = 49.60 Hz, 1H) 1.93−1.61 (dm, J = 113.41 Hz, 12H, $C\mathit{H_2}CH_3$), 1.12−0.97 (m, 18H, $CH_2C\mathit{H_3}$), 0.67−0.55 (m, 1H). ^{13}C NMR (75.47 MHz, CD_2Cl_2): 147.77 (s), 144.88 (s), 129.33 (s), 128.69 (s), 128.52 (t, J_{PC} = 4.23 Hz), 128.05 (s), 127.85 (s), 127.42 (s), 126.62 (s), 125.93 (s), 125.60 (s), 14.32 (m, $\mathit{C}H_2CH_3$), 8.05 (m, $CH_2\mathit{C}H_3$). ^{31}P NMR (101.25 MHz, CD_2Cl_2): 14.1 (s, $^1J_{PtP}$ = 2661 Hz).

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Supporting Information Available: Details for the X-ray structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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