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Complexes of Platinum(II) and Palladium(II) with the 2,2'-Biphenyldiyl Dianion as a σ-Bonded Chelate Ligand

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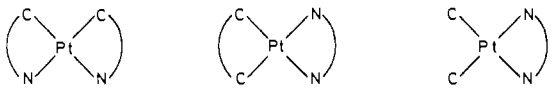
Pt(bph)(bpy) (A) and Pd(bph)(bpy) (B), where bph^{2-} is the twofold-deprotonated, chelating biphenyl ligand and bpy is 2,2'-bipyridine, are air-stable, crystalline compounds. They can be prepared in low-temperature reactions from *cis*-$PtCl_2(Et_2S)_2$ and from *trans*-$PdCl_2(Et_2S)_2$, respectively, in two steps. *trans*-$PtCl_2(Et_2S)_2$ yields in the same reaction sequence $Pt(Hbph)_2(bpy)$ (C). A is an isomer of the previously prepared $Pt(phpy)_2$ (D), where $phpy^-$ is C-deprotonated phenylpyridine. A has a strong absorption in the visible region and shows a marked solvatochromism. It is assigned to a Pt → bpy MLCT transition; the second band, in the UV region, is assigned to a Pt → bph MLCT transition. A shows a reversible reduction wave in the cyclic voltammogram, at a potential that is 500 mV less negative than that for D. A and C undergo thermal and photochemical oxidative-addition reactions similar to those of D, yielding Pt(IV) complexes. In view of the instability of $Pd(ph)_2(bpy)$, B is a remarkably stable compound. It reacts with halocarbons, either thermally or photochemically (UV irradiation), to give Pd(II) complexes having a substituted biphenyl ligand coordinated through one carbon.

Introduction[1]

In our laboratories a series of complexes of Pt(II)[2] and Pd(II)[3] containing two cyclometalated rings (I) was recently prepared.



I II III

The chelating C,N ligands are, e.g., deprotonated 2-phenylpyridine or 2-thienylpyridine. Such complexes show interesting emission properties[4,5] and a marked propensity[6-8] to undergo thermal or photochemical oxidative-addition reactions. In the present paper, we report the preparation of complexes having structure II, where (C···C) is the dianion of 2,2'-biphenyl (bph), an isomeric form of I. Some related compounds are also described. Several properties of the new compounds are investigated. Compounds containing the Pt(bph) moiety have been prepared before,[15] and the cationic Au(III) complex analogous to structure II has been reported.[9] The former were species having π-ligands bound to the central metal, e.g. cyclooctadiene, and they are therefore not directly comparable with compounds having structure II. One can compare the complexes of structure II with those of structure III, which were reported by Chaudhury and Puddephatt[10] and Steele and Vrieze.[11] "C–" is a monodentate σ-bonded alkyl or aryl group. In structure II, the aryl groups are necessarily approximately coplanar with the plane of the complex, in contrast to compounds of structure III.[12] There are many similarities between the compounds of the three series but also some marked differences. An important one is the possibility to prepare Pd(bph)(bpy) (structure II), whereas $Pd(ph)_2(bpy)$ (structure III) cannot be prepared[13] with unsubstituted phenyl due to formation of biphenyl.

Experimental Section

Materials. 2,2'-Dibromobiphenyl,[14] 2,2'-dilithiobiphenyl,[15] $PtCl_2((C_2H_5)_2S)_2$,[16] and $PdCl_2((C_2H_5)_2S)_2$[17] were prepared by published procedures. Solvents were dried prior to use by standard techniques. Reactions involving lithium reagents were carried out under a nitrogen atmosphere by using Schlenk tube techniques.

Measurements. Electronic spectra were recorded with a Perkin-Elmer 555 spectrometer. ^1H and ^{13}C NMR spectra were collected with a Bruker AM-360 spectrometer (internal standard TMS). Mass spectra were obtained with a 7070 E VG Instruments spectrometer, and IR spectra were measured with a 683 Perkin-Elmer spectrometer. Electrochemical measurements were carried out with a Metrohm Polarecord 506 coupled with a VA scanner, Model E 612.

(a) Preparation of $[Pt(bph)(SEt_2)_2]_2$. A solution of Li_2bph (from 840 mg (2.7 mmol) of 2,2'-dibromobiphenyl) in ether (20 mL) is added dropwise to a stirred suspension of *cis*-$PtCl_2(SEt_2)_2$ (600 mg, 1.34 mmol) in ether (20 mL) at −10 °C. The reaction mixture is stirred for 1 h at −10 °C and again for 1 h at 0 °C and than hydrolyzed with 10 mL H_2O. Separation of the organic layer, extraction with CH_2Cl_2, evaporation, purification with flash chromatography (silica gel, CH_2Cl_2:hexane = 3:2), and recrystallization (CH_2Cl_2/pentane) give 100 mg of $[Pt(bph)(Et_2S)_2]_2$ as a pale yellow crystalline product.

^1H NMR ($CDCl_3$; ppm): 7.34 (dd, J = 7.5 Hz, J = 1.3 Hz, 2 H, H–C(6)), 7.05 (ddd, J = 7.4 Hz, J = 1.10 Hz, 2 H, H–C(5)), 7.01 (dd, J = 7.4 Hz, J = 1.1 Hz, 2 H, H–C(3)), 6.91 (ddd, J = 7.4 Hz, J = 1.3 Hz, 2 H, H–C(4)), 3.85 (q, J = 7.3 Hz, J(Pt–H) = 40 Hz, 4 H, $-CH_2$), 1.78 (t, J = 7.3 Hz, 6 H, CH_3). IR (KBr; cm^{-1}): 3067 m, 3058 m, 2982 m, 2934 m, 1583 w, 1469 m, 1459 m, 1427 s, 1378 m, 1245 m, 1180 w, 1056 m, 1033 m, 1021 m, 1004 w, 975 w, 781 m, 734 s, 700 s, 669 w, 490 w, 440 w. Electronic spectrum (CH_2Cl_2): λ_{max} (nm) = 235 (ϵ = 45 700 M^{-1} cm^{-1}), 252 (37 500), 266 (37 200), 272 s (36 200), 292 s (24 500), 310 (24 450), 340 (22 500). Anal. Calcd for $C_{32}H_{36}S_2Pt_2$: C, 43.93; H, 4.15. Found: C, 43.92; H, 3.99.

(b) Preparation of Pt(bpb)(bpy). $[Pt(bph)(SEt_2)]_2$ (40 mg, 0.05 mmol) is added to melted bpy (500 mg, 3.2 mmol) at +80 °C. The color of the solution turns rapidly deep red. After being stirred for 10 min under reduced pressure, the reaction mixture is cooled with an ice bath and the solid reaction mixture is dissolved in CH_2Cl_2. Upon addition of hexane, Pt(bph)(bpy) precipitates. Recrystallization (CH_2Cl_2/pentane) gives 30 mg of a deep red crystalline product.

^1H NMR ($CDCl_3$; ppm): 9.65 (d, broad, J = 5.6 Hz, J(Pt–H) = 16.11 Hz, 2 H, H–C(6)), 8.16 (ddd, J = 7.5 Hz, J = 2.6 Hz, 2 H, H–C(4)), 8.11 (dd, J = 7.5 Hz, J = 1.4 Hz, 2 H, H–C(3)), 7.64 (ddd J = 7.5 Hz, J = 5.6 Hz, J = 2.6 Hz, 2 H, H–C(5)), 7.46 (dd, J = 7 Hz,

(1) The following abbreviations are used throughout: bph^{2-}, twofold deprotonated biphenyl; $Hbph^-$, deprotonated biphenyl; $phpy^-$, deprotonated phenylpyridine; bpy, 2,2'-bipyridine. Charges are omitted if the ligands are bound to a metal.
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J(Pt–H) = 56 Hz, 2 H, H–C(3′)), 7.39 (dd, J = 7.2 Hz, J = 1.6 Hz, 2 H, H–C(6′)), 7.01 (ddd, J = 7.2 Hz, J = 1.4 Hz, 2 H, H–C(5′)), 6.91 (ddd, J = 6.9 Hz, J = 1.5 Hz, 2 H, H–C(4′)). IR (KBr; cm^{-1}): 3074 w, 3047 w, 1606 m, 1469 m, 1445 s, 1417 s, 1314 w, 1239 w, 1157 w, 921 w, 755 m, 740 m, 727 s, 669 w, 507 w, 494 w, 414 w. Mass spectrum: m/e 503 (M^+). Electronic spectrum (CH_2Cl_2): λ_{max} (nm) = 248 s (ϵ = 26 160 M^{-1} cm^{-1}), 260 (25 900), 292 (17 700), 308 s (13 430), 320 s (9100), 440 (4890). Anal. Calcd for $C_{22}H_{16}N_2Pt$: C, 52.48; H, 3.20; N 5.56. Found: C, 52.02; H, 3.13; N, 5.39.

(c) Preparation of Pt(Hbph)$_2$(bpy). *trans*-$PtCl_2(SEt_2)_2$ (600 mg, 1.34 mmol) is treated as described in part a. A 350-mg yield of a white crystalline product is obtained. Without further characterization the product is mixed with melted bpy (800 mg, 5.13 mmol) and treated as described in part b. Crystallization (CH_2Cl_2/pentane) yields 250 mg of a red/orange crystalline product.

^1H NMR ($CDCl_3$; ppm): 8.44 (dd, broad, J = 5.4 Hz, J = 1.5 Hz, 2 H, H–C(6)), 8.00 (ddd, J = 7.5 Hz, J = 1.5 Hz, 2 H, H–C(4)), 7.92 (dd, J = 7.8 Hz, J = 1.3 Hz, 2 H, H–C(3)), 7.80 (dd, large, J = 5.5 Hz, 4 H, H–C(8′)), 7.27 (ddd, J = 7.5 Hz, J = 5.5 Hz, J = 1.3 Hz, 2 H, H–C(5)), 7.14 (dd, J = 7.5 Hz, J = 1.4 Hz, 2 H, H–C(6′)), 7.10–7.06 (m, 6 H, H–C(9′), H–C(10′)), 6.90 (ddd, J = 7.10 Hz, J = 1.5 Hz, 2 H, H–C(5′)), 6.81 (dd, J = 7.5 Hz, J = 1.3 Hz, 2 H, H–C(3′)). IR (KBr; cm^{-1}): 3074 w, 3043 m, 3033 m, 1606 m, 1573 m, 1493 m, 1471 m, 1448 s, 1416 m, 1386 m, 1315 m, 1315 w, 1248 w, 1172 w, 1154 w, 1108 w, 1066 w, 1033 m, 1006 w, 994 w, 900 m, 779 w, 743 s, 728 s, 696 s, 655 w, 613 w, 561 w, 523 w, 500 w, 469 w, 421 w. Mass spectrum: m/e 656 (M^+). Electronic spectrum (CH_2Cl_2): λ (nm) = 289 (ϵ = 21 300 M^{-1} cm^{-1}), 276 s (1600), 458 (2400). Anal. Calcd for $C_{34}H_{26}N_2Pt$: C, 62.09; H, 3.98; N, 4.26. Found: C, 61.77; H, 3.91; N, 4.21.

(d) Preparation of Pd(bph)(bpy). A solution of Li_2bph (from 840 mg (2.7 mmol) of 2,2′-dibromobiphenyl) in ether (20 mL) is added dropwise to a stirred suspension of $PdCl_2(Et_2S)_2$ (400 mg, 1.4 mmol) in ether (20 mL) at −78 °C. The dry ice/acetone cooling bath is replaced by an ice/NaCl bath. Within one minute a clear, yellow-orange solution is obtained, which is stirred for 5 min at −10 °C then cooled to −78 °C. Bpy (500 mg, 3.2 mmol) is added, and then the suspension is stirred for 15 min at −10 °C and finally hydrolized with 10 mL of H_2O. Separation of the organic layer, extraction with CH_2Cl_2, evaporation, and recrystallization from CH_2Cl_2/ether gives 140 mg of yellow needles.

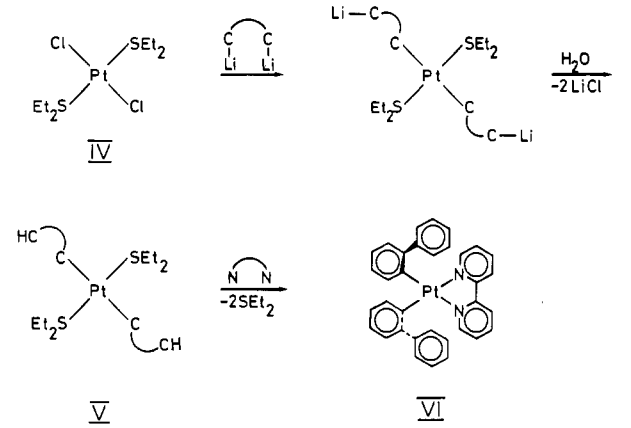
^1H NMR ($CDCl_3$; ppm): 9.28 (d, broad, J = 5.1 Hz, 2 H, H–C(6)), 8.48, (d, large, J = 7.9 Hz, 2 H, H–C(3)), 7.99 (ddd, J = 7.9 Hz, J = 1.5 Hz, 2 H, H–C(4)), 7.57 (ddd, J = 7.5 Hz, J = 5.4 Hz, J = 1.4 Hz, 2 H, H–C(5)), 7.46 (d, broad, J = 6.8 Hz, 2 H, H–C(3′)), 7.37 (dd, J = 7.4 Hz, J = 1.4 Hz, 2 H, H–C(6′)), 7.04 (ddd, J = 7.4 Hz, J = 1.1 Hz, 2 H, H–C(5′)), 6.92 (ddd, J = 7.4 Hz, J = 1.4 Hz, 2 H, H–C(4′)). ^{13}C NMR ($CDCl_3$; ppm): 163.14 (1 C, C(2)), 157.48 (1 C, C(2′)), 155.32 (1 C), 151.41 (1 C), 138.08 (1 CH), 133.97 (1 CH), 125.88 (1 CH), 124.88 (1 CH), 124.26 (1 CH), 122.16 (1 CH), 119.76 (1 CH). IR (KBr; cm^{-1}): 3040 w, 1602 m, 1575 w, 1563 w, 1469 m, 1442 s, 1424 w, 1415 w, 1313 w, 1239 w, 1160 m, 1044 m, 752 s, 725 s, 697 w, 615 w, 478 w, 431 w, 410 w. Electronic spectrum (CH_2Cl_2): λ_{max} (nm) = 248 (ϵ = 28 850 M^{-1} cm^{-1}), 156 s (27 330), 292 (13 900), 340 (4970), 360 s (3700). Anal. Calcd for $C_{22}H_{16}N_2Pd$: C, 63.37; H, 3.88; N, 6.75. Found: C, 63.41; H, 3.81; N, 6.68.

(e) Reaction of Pt(bph)(bpy) with CH_3I. In the dark CH_3I (1 mL), freshly distilled, is added to a stirred solution of Pt(bph)(bpy) (20 mg) in 20 mL of CH_2Cl_2. Decolorization of the red solution occurs. After the reaction mixture has been stirred for 10 min, the volume of the solution is reduced. Upon addition of ether and cooling, yellow crystals of Pt(bph)(bpy)CH_3I are obtained.

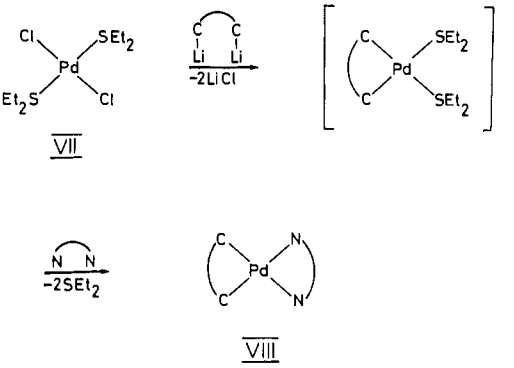
^1H NMR ($CDCl_3$; ppm): 9.19 (dd, J = 5.3 and 1.0 Hz, J(Pt–H) = 12.5 Hz, 1 H, H–C(6a)), 8.78 (dd, J = 7.6 and 1.2 Hz, J(Pt–H) = 42.6 Hz, 1 H, H–C(3′a)), 8.31 (d, J = 8.0 Hz, 1 H, H–C(3a)), 8.24–8.19 (m, 2 H, H–C(4a), H–C(6b)), 8.14 (d, J = 7.1 Hz, 1 H, H–C(3b)), 7.89–7.83 (m, 2 H, H–C(4b), H–C(5a)), 7.49 (dd, J = 7.6 and 1.5 Hz, 1 H, H–C(6′a)), 7.37 (dd, J = 7.6 and 1.5 Hz, 1 H, H–C(6′b)), 7.26 (ddd, J = 7.3, 5.4, and 1.1 Hz, 1 H, H–C(5b)), 7.18, ddd, J = 7.6 and 1.2 Hz, 1 H, H–C(5′a)), 7.05 (ddd, J = 7.6 and 1.5 Hz, 1 H, H–C(4′a)), 6.92 (ddd, J = 7.6 and 1.1 Hz, 1 H, H–C(5′b)), 6.55 (ddd, J = 7.6 and 1.5 Hz, 1 H, H–C(4′b)), 5.80 (dd, J = 7.6 and 1.1 Hz, J(Pt–H) = 46.6 Hz, 1 H, H–C(3′b)), 1.57 (s, J(Pt–H) = 69.4 Hz, 3 H, $-CH_3$). Anal. Calcd for $C_{23}H_{19}IN_2Pt$: C, 42.80; H, 2.97; N, 4.34. Found: C, 42.92; H, 3.03; N, 4.44.

(f) Reaction of Pd(bph)(bpy) with CH_3I. In the dark CH_3I (1 mL) is added to a stirred solution of Pd(bph)(bpy) (20 mg) in 20 mL of CH_2Cl_2. The reaction mixture is stirred for 12 h. The product is separated from the Pd(bph)(bpy) still present, with flash chromatography (silica gel, hexane:ether:CH_2Cl_2 = 5:5:6). Recrystallization from CH_2Cl_2 yielded yellow needles of Pd((bph)CH_3)(bpy)I.

Scheme I



Scheme II



^1H NMR ($CDCl_3$, 50 °C; ppm): 9.54 (d, J = 4.9 Hz, 1 H, H–C(6a)), 7.95 (d, broad, J = 5.0 Hz, 2 H, H–C(3a), H–C(3b)), 7.90–7.87 (m, 2 H, H–C(4a), H–C(4b)), 7.94 (d, J = 5.6 Hz, 1 H, H–C(6b)), 7.62 (d, large, J = 7.5 Hz, 1 H, H–C(3′)), 7.38 (ddd, J = 6.3, 5.0, and 1.3 Hz, 1 H, H–C(5a)), 7.35 (ddd, J = 7.3, 4.5, and 4.7 Hz, 1 H, H–C(5b)), 7.10–6.8 (m, 7 H, H–C(4′–12′)), 2.2 (s, 3 H, $-CH_3$). Electronic spectrum (CH_2Cl_2): λ_{max} (nm) = 300, 360 s. Anal. Calcd for $C_{23}H_{19}IN_2Pd$: C, 49.62; H, 3.44; N, 5.03. Found: C, 49.51; H, 3.40; N, 5.15.

(g) Photoreaction of Pd(bph)(bpy) with CH_2Cl_2. A solution of Pd(bph)(bpy) (20 mg) in CH_2Cl_2 (30 mL, deaerated with argon) is irradiated with a HPK 125-W Philips UV lamp for 30 min. A yellow microcrystalline powder identified as Pd(bpy)Cl_2 is obtained.

Electronic spectrum (CH_2Cl_2): λ_{max} (nm) = 261, 306, 315.

Results and Discussion

Synthesis. Reaction of $PtCl_2(SEt_2)_2$ with Li_2bph and bpy. The preparation of dimeric complexes $[Pt(ph)_2SR_2]_2$ with phenyllithium and *cis*-$PtCl_2(SR_2)_2$ has been reported by Steele and Vrieze.[11] In the same manner *cis*-$PtCl_2(SEt_2)_2$ reacts with an excess of Li_2bph, giving after hydrolysis $[Pt(bph)(SEt_2)]_2$. The rapid substitution of both bridging diethyl sulfide ligands in melted bpy leads to the formation of Pt(bph)(bpy).

The reaction of *trans*-$PtCl_2(SEt_2)_2$ with phenyllithium reported by Steele and Vrieze[11] gives a mixture of 55% of $[Pt(ph)_2(SEt_2)]_2$ and 20% of $Pt(ph)_2(SEt_2)_2$. Supposing that *trans*-$PtCl_2(SEt_2)_2$ would react with Li_2bph in the same manner, we obtained a white crystalline product, which was used without characterization in the next step. Diethyl sulfide is easily replaced by bpy, forming the unexpected product Pt(Hbph)$_2$(bpy). As possible reaction path is given in Scheme I.

Reaction of *trans*-$PdCl_2(SEt_2)_2$ with Li_2bph and bpy. *cis*-$(aryl)_2PdL_2$ compounds are unknown. Reaction of Li(ph) with *trans*-$PdCl_2(SEt_2)_2$ results in complete decomposition at −50 °C with formation of biphenyl.[18] Similarly, Steele and Vrieze[11] failed to isolate $Me_2Pd(SEt_2)_2$ because the product decomposes at room temperature.

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Table I. Variation of the Position of the First Two Absorption Bands in the Electronic Spectra of Three Pt Complexes and One Pd Complex in Solvents of Different Polarity[a]

	Pt(bph)(bpy)		Pd(bph)(bpy)		$Pt(Hbph)_2(bpy)$		$[Pt(bph)(SEt_2)]_2$	
solvent	λ_1	λ_2	λ_1	λ_2	λ_1	λ_2	λ_1	λ_2
methanol	23.92	32.89	29.58	34.48				
acetonitrile	23.47	28.25	28.90	29.94	22.52	27.17	31.15	33.55
acetone	22.93	28.41	29.09	29.24	22.12	26.59	29.76	
chloroform	22.42	30.49	28.09	29.32	21.18	28.09	29.41	32.26
toluene	21.93	29.76	26.59	29.41	20.66	25.77	29.41	32.36
	20.66					27.78		

[a] λ 1000 cm^{-1}.

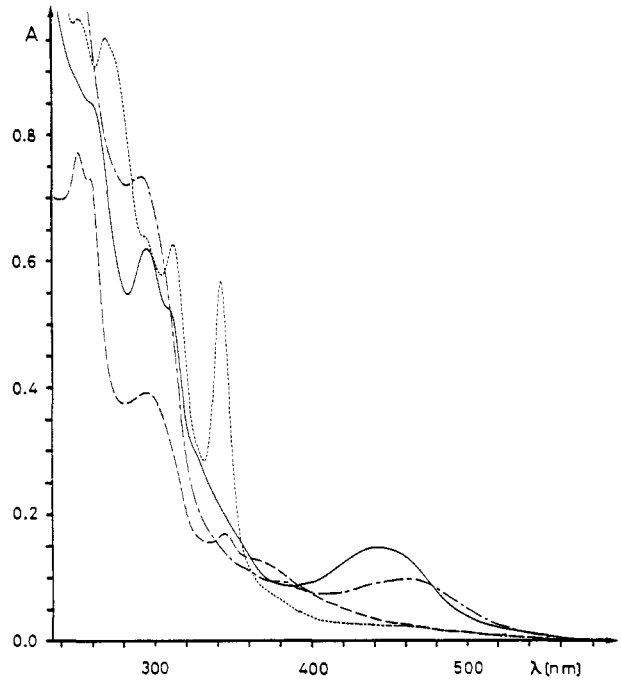


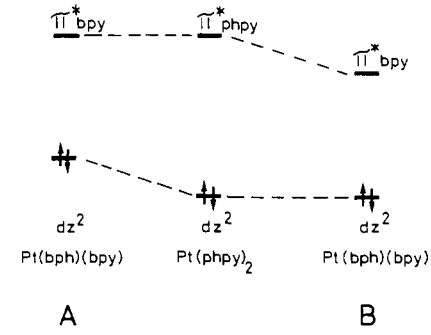
Figure 1. UV/vis spectra in CH_2Cl_2: (–) Pt(bph)(bpy), 3.5×10^{-5} M; (---) Pd(bph)(bpy), 2.8×10^{-5} M; (···) $[Pt(bph)(Et_2S)]_2$, 2.4×10^{-5} M; (·–·) $Pt(Hbph)_2(bpy)$, 3.4×10^{-5} M.

The preparation of Pd(bph)(bpy) follows Scheme II. *trans*-$PdCl_2(SEt_2)_2$ reacts rapidly with Li_2bph, while the temperature of the reaction mixture is raised from −70 to −10 °C. Without isolation of the intermediate $Pd(bph)(SEt_2)_2$ (which decomposes to black Pd if the solution is kept for more than ca. 15 min at a temperature of −10 °C), the solution is again cooled to −70 °C, and bpy is added at this temperature. During the process of raising the temperature again to −10 °C, bpy substitutes the thioether to form the stable Pd(bph)(bpy). The decomposition of Pd(bph)$(SEt_2)_2$ is slower compared to that of $Pd(ph)_2(SEt_2)_2$ because elimination through C–C bond formation, as it occurs in the diphenyl complex,[18] is no longer possible.

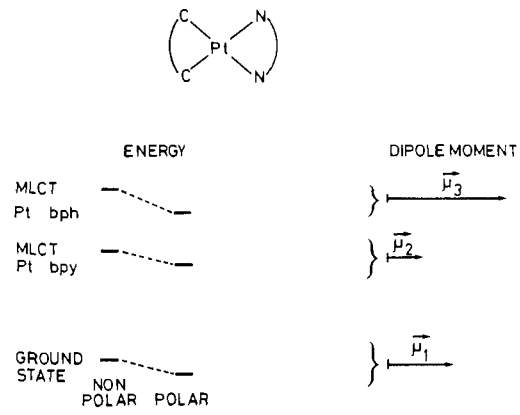
Electronic Spectra. Figure 1 gives the absorption spectra of several complexes containing the (2,2′-biphenyldiyl dianion)metal moiety. From the positions which the ligands probably occupy in the spectrochemical series, it is to be expected that no d–d transitions will lie in the visible or in the near-UV region (λ <300 nm) of the spectrum. The bands observed in this region are therefore due to either charge-transfer or ligand-centered transitions.

Pt(bph)(bpy) has a strong absorption band in the visible region, (band 1, ϵ = 5000) that shows a marked solvent dependence (Table I). This band, which disappears completely in the products of the oxidative addition (vide infra), is assigned to a Pt → bpy MLCT transition. The energy is ca. 10% lower than that of the corresponding band in the isomer $Pt(phpy)_2$ in dichloromethane,[1] and the solvatochromic range is nearly three times larger. This bathochromic shift can be due either to an increase in the energy of the departure orbital for the ^{1}MLCT transition or a decrease of the energy of the arrival orbital or both. The former is the d_{z^2} orbital, σ^* toward two sp^2 carbon anions and two sp^2 nitrogen atoms in both complexes; the latter two are the π^* orbitals of bpy and $phpy^-$, respectively. From this consideration, correlation B is more probable than correlation A in Scheme III, in agreement with the electrochemical behavior (vide infra).

Scheme III



Scheme IV



It is in agreement with the assignments of Chaudhury and Puddephatt[10] in the spectra of dialkyl- and diaryl-Pt(bpy) complexes, and it occurs also in $Pt(Hbph)_2(bpy)$ (Table I). The second band shows also a solvent dependence (Table I) but with an opposite sign as compared to band 1.

With a tentative assignment of the latter to a Pt → bph MLCT transition, the solvent polarity dependences can be explained in terms of a simple model (Scheme IV).

The rationale behind this model is based on the estimated dipole moments of the ground and the excited states. In the ground state, the dipole moment is believed to point in the direction of the bpy ligand, bisecting the N–Pt–N angle. The direction is given by symmetry and the sign by the formal negative charges on the bph^{2-} ligand. A Pt → bpy MLCT transition displaces negative charge to the bpy ligand, reducing therefore strongly the dipole moment in the excited state. A Pt → bph MLCT on the other hand increases the dipole moment as compared to the ground state. The situation is depicted in Scheme IV, where the corresponding energy levels are indicated for nonpolar and polar surroundings, respectively.

The much weaker dependence of band 1 of solvent polarity in $Pt(phpy)_2$, in which the ground-state dipole moment is, for sym-

Table II. ^{1}H NMR Shifts (ppm) in Pt and Pd Complexes and in the Free Ligands

compd[e]	chem shift H–C(6)	chem shift H–C(3')	ref
bpy	8.67		
Hphpy	8.69	7.49	
Br_2bph		7.25	
Pt(bpy)Cl_2	9.52		
Pt(bpy)Me_2	9.16		20
Pt(bph)(bpy)	9.65[a]	7.46[b]	
Pd(bph)(bpy)	9.28	7.46	
[Pt(bph)SEt_2]$_2$		7.01[c]	
Pt(phpy)$_2$[d]	8.79	8.08	1
Pd(phpy)$_2$	8.59	8.08	3
Pt(Hpbh)$_2$(bpy)	8.44[c]	7.14[c]	

[a] J_{Pt-H} = 16.1 Hz. [b] J_{Pt-H} = 56 Hz. [c] Coupling constant not observable. [d] For Pt(phpy)$_2$, $J_{H-C(6)}$ = 18 Hz and $J_{H-C(3')}$ = 54.3 Hz. [e] Structures:

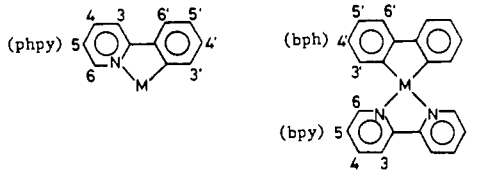


Table III. Reduction/Oxidation Potentials (Cyclic Voltammetry) in Acetonitrile Solution[a]

complex	potential, V vs. SCE E	E_p	ref
Pt(phpy)$_2$	−1.94[b]	0.07[c]	2
Pt(bpy)$_2$(PF_6)$_2$[d]	−0.97[b]		2
	−1.51[b]	0.07	
	−2.53[b]	0.06	
Pt(bph)(bpy)	−1.47[b]	0.07[c]	
Pt(Hbph)$_2$(bpy)	−1.50[b]	0.07[c]	

[a] Supporting electrolyte is 0.1 M tetraethylammonium perchlorate. [b] Reversible. [c] Irreversible. [d] Solvent DMF.

metry reasons, pointing between the two ligands, is also in qualitative agreement with this model. The dipole moment in the excited state lies most likely in a different direction, diminishing therewith the influence of solvation by a polar solvent.

The attribution of the second band (λ_2, Table I) in Pt(bph)(bpy) to a Pt → bph MLCT transition is corroborated by the observation of a band at about the same energy in [Pt(bph)(SEt_2)]$_2$ (Table I).

As expected for MLCT transitions, the bands are strongly shifted to higher energies in the Pd complexes as compared to the Pt species (Table I). A detailed discussion is more difficult, because ligand-centered transitions most likely interfere with the charge-transfer bands.

Electrochemistry. The electrochemical behaviors of Pt(bph)(bpy) and Pt(Hbph)$_2$(bpy), as observed by cyclic voltammetry in acetonitrile, are basically very similar to that of Pt(phpy)$_2$ (Table III). In Pt(bph)(bpy) and in Pt(Hbph)$_2$(bpy), it is however displaced by about 500 mV to a less negative potential than in Pt(phpy)$_2$. Moreover the two complexes with bpy as ligand have reduction potential very similar to that of the first reversible step in Pt(bpy)$_2^{2+}$ (Table III). This reversible reduction can be attributed to a bpy-centered uptake of one electron. This is in complete agreement with correlation B in Scheme III, developed for the interpretation of the UV/vis spectra.

NMR. Table II shows NMR data of protons in a position ortho to the M–C or M–N bonds for some Pt and Pd compounds.

Upon cyclometalation the signals of protons H–C(6) in Pt(bph)(bpy) and Pd(bph)(bpy) exhibit a strong downfield shift ($\Delta\delta \sim 0.98$ for Pt and 0.59 for Pd) caused by a strong interaction between the N donor atoms of bpy and the metal center. A through-space shielding caused by an adjacent aromatic ring (bph) and a π-back-bonding from the electron-rich metal to the bpy ligand would produce an upfield shift as Selbin[19] observed in Pd(phpy)(dtc) (dtc = dithiocarbamate) (the protons H–C(6) and H–C(3') show upfield shifts of 0.3 and 0.4 ppm, respectively). The π effect must be smaller than the one observed for the signal of H–C(6) in M(phpy)$_2$ because in the latter the π-back-bonding coming from the phenyl ring is delocalized through the whole system in the pyridine ring.

The shift of the signal of H–C(3') is little influenced by complexation. The σ effect, which displaces the signal downfield, is here opposed by a π effect.

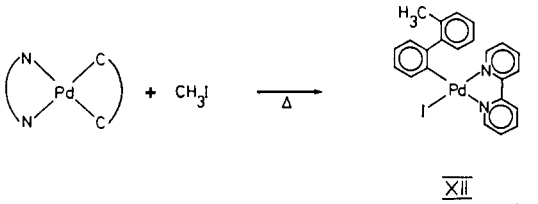
The signals of H–C(3) of (Pt(bph)SEt_2)$_2$ exhibit a dramatic upfield shift. The main cause is probably a strong π-back-bonding, due to the σ-donor strength of S.

Reactivity. The reactivity of Pt(II)– and Pd(II)–diaryl and –dialkyl complexes with halocarbons is of recent interest.[6-8,21-24] The basic reaction type is oxidative addition, either thermally[21,23,24] or photochemically[6-8,22] activated. The latter has been shown to proceed, at least partially, via one or more excited states above the lowest one,[8] but it is nevertheless remarkably stereoselective in several cases.

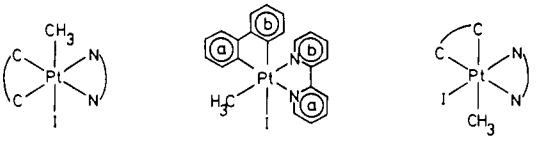
The reactivity of Pt(bph)(bpy) and Pd(bph)(bpy) toward halocarbons is examined in the present paper in a general way. More detailed research, concerning mechanisms of various types of reactions, is in progress, and the results will be published in due course.

Pt(bph)(bpy) reacts in the dark with CH_3I to give one principal product, which was identified by ^{1}H NMR spectroscopy. The nonequivalence of all aromatic protons (in bph *and* bpy) indicates cis addition, i.e. structure X or XI of the three possible isomers.

Scheme V



XII



IX X XI

Since the $^2J(^{195}Pt–H(CH_3))$ coupling constant of 69.4 Hz is very similar to that in other complexes,[25] where CH_3 is trans to a N-donor, we attribute structure X to the product. Formation of mainly the cis adduct is a noteworthy difference from the behavior of Pt(ph)$_2$(bpy)$_2$,[21] where only trans addition takes place, and also from Pt(phpy)$_2$, where a cis/trans mixture is obtained.

Photochemically activated oxidative addition seems to follow a similar reactivity pattern in Pt(bph)(bpy) and in Pt(phpy)$_2$, i.e. no addition of CH_2Cl_2 in the dark and reaction with a relatively high quantum yield under irradiation with visible light. The stereoselectivity seems to be somewhat less pronounced in Pt(bph)(bpy) compared to Pt(phpy)$_2$.

The corresponding reactions of the Pd complexes are quite different, due to the instability of Pd(IV) compounds. Pd(bph)(bpy) reacts thermally with CH_3I but not with chlorinated halocarbons such as, e.g., CH_2Cl_2, in which it can be refluxed for

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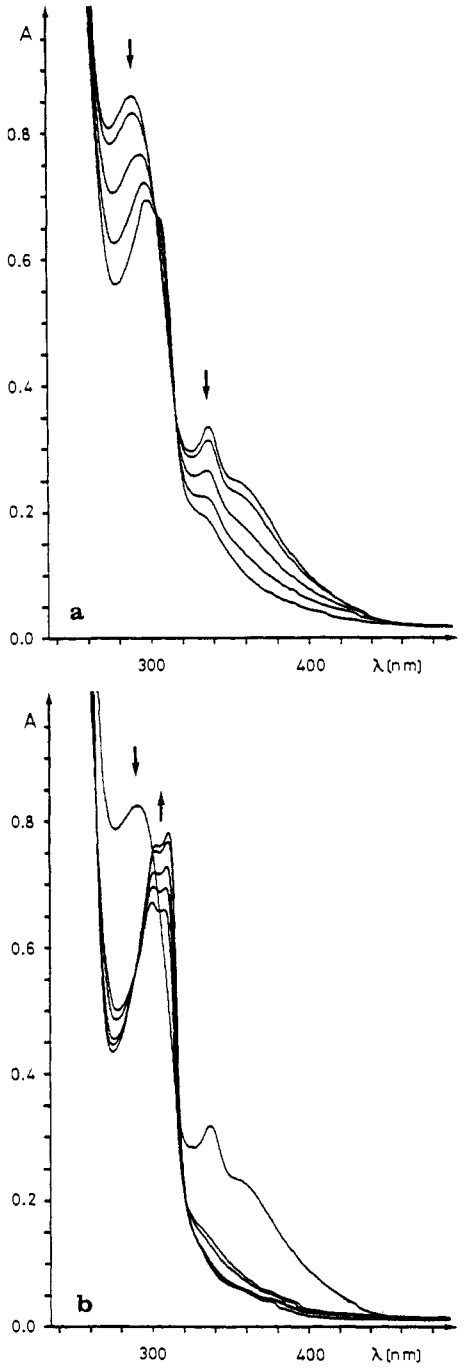
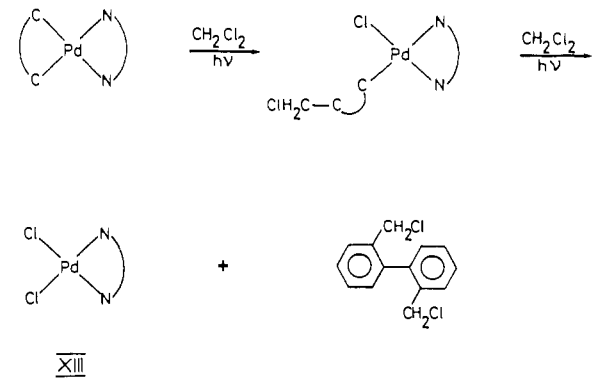


Figure 2. UV/vis spectra: (a) taken during the first step of the photoreaction of Pd(bph)(bpy) in CH_2Cl_2 (time interval between two spectra ca. 2 s); (b) taken during the second step of the photoreaction of Pd(bph)(bpy) in CH_2Cl_2 (time interval between two spectra ca. 15 s).

12 h without decomposition. The reaction with CH_3I is relatively slow, as compared with that of Pt(bph)(bpy) (ca. 12 h, room temperature) and not quantitative. The product is a Pd(II) complex, with one *o*-tolyl-2-phenyl) ligand (XII) (Scheme V).

The structure was deduced from the NMR spectrum. The chemical shift of the protons of the methyl group is characteristic

Scheme VI



XIII

for a methyl belonging to a tolyl group (chemical shifts for methyl groups attached to Pd(IV) are in the range 1.85–1.14 ppm[26]). The long reaction period does not allow us to isolate a Pd(IV) compound, considering that $PdI(CH_3)_3(bpy)$[26] decomposes at room temperature within 20–30 min. to give $PdI(CH_3(bpy))$ and ethane.

There have been two different mechanisms proposed for the reaction of methyl iodide with diaryl- and dialkyl–Pd(II) complexes. Moravskiy and Stille[24] proposed a reaction sequence of oxidative addition to Pd(IV) with subsequent reductive elimination, whereas Yamamoto et al.[23] found evidence for a reductive elimination process involving intermolecular exchange of organic groups with a Pd(0) compound as intermediate.

Without carrying out a detailed study of the reaction mechanism, so far, we can rule out almost certainly the sequence involving a Pd(0) complex in our case. The main reasons for this conclusion are that (i) the biphenyldiyl ligand remains bound to the palladium and (ii) some of the intermediates (especially the binuclear exchanging species)[23] mentioned by Yamamoto are highly improbable for the chelated biphenyl compound.

The sequence proposed by Stille et al.[24] is, on the other hand, quite possible for Pd(bph)(bpy).

Pd(bph)(bpy) is photoreactive in CH_2Cl_2 and $CHCl_3$ under UV irradiation. The photoreaction can be follow by UV/vis spectroscopy. Upon irradiation (12 s) (Figure 2a), the band at 292 nm is shifted to 300 nm and the band at 340 nm disappears with an isosbestic point at 320 nm. The spectrum of the product is very similar to the spectrum of $Pd((bph)CH_3)(bpy)I$. Upon longer irradiation (75 s) a second photoreaction occurs (Figure 2b), the band at 300 nm is shifted to 304 nm, and a novel band at 312 nm appears. Two isosbestic points at 292 and 526 nm are observed. The spectrum of the product is identical with the spectrum of $Pd(bpy)Cl_2$. Scheme VI represents a possible reaction pathway: it involves a sequence similar to the oxidative addition with CH_3I in the first step, followed by a second identical step.

Acknowledgment. This work was supported by the Swiss National Science Foundation.

Registry No. $[Pt(bph)(SEt_2)_2]_2$, 110077-25-3; Pt(bph)(bpy), 110077-26-4; $Pt(Hbph)_2(bpy)$, 110077-27-5; Pd(bph)(bpy), 110077-28-6; $Pt(bpy)(bpy)CH_3I$, 110077-29-7; $Pd((bpy)CH_3)(bpy)I$, 110077-30-0; Li_2bph, 16291-32-0; *cis*-$PtCl_2(SEt_2)_2$, 15442-57-6; *trans*-$PtCl_2(SEt_2)_2$, 15337-84-5; $PdCl_2(Et_2S)_2$, 14873-91-7; $Pd(bpy)Cl_2$, 14871-92-2; Hphpy, 1008-89-5; Br_2bpy, 13029-09-9.

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