= 119 Hz, $SiMe_3$), 29.3 (q, $^1J_{CH}$ = 124 Hz, CH_3), 110.2 (d, $^1J_{CH}$ = 173 Hz, Cp), 122.4 (d, $^1J_{CH}$ = 148 Hz, =CH–), 126.0, 127.6, 128.0 (each d, Ph), 145.1 (s), 151.0 (s), 191.8 (s), 199.3 (s).

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Supplementary Material Available: Details on the X-ray data collection and structure determination of **3a** and **3c** and lists of bond lengths and angles, atomic fractional coordinates, and thermal parameters of **3a** and **3c** (13 pages); listings of observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

Communications

Phase-Transfer-Catalyzed P–C Bond Cleavage in Platinum Bis(diphenylphosphino)methane Complexes under Exceedingly Mild Conditions

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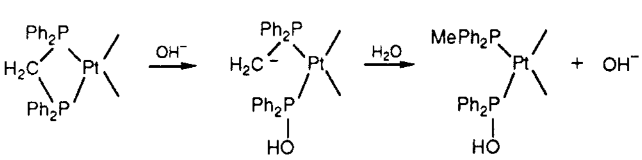
Summary: The reaction of [$Pt(dppm)Cl_2$] (dppm = $Ph_2PCH_2PPh_2$) with [$S(O)Me_3$]Cl under basic phase-transfer-catalyzed conditions gave the complex {$Pt(PPh_2Me)[PPh_2(OH)][(CH_2)_2S(O)Me]$}Cl, which contains a bidentate sulfur ylide and two monodentate phosphine ligands. The latter was produced by the facile base hydrolysis of the dppm ligand, a reaction that is general for other Pt–dppm complexes.

In recent years, there has been increasing interest in the use of phase-transfer catalysis (PTC) in organometallic chemistry.[1] We have previously shown that sulfur ylide complexes of palladium could be prepared using the biphasic PTC/OH^- technique.[2] We have further pointed out that sulfur ylide complexes of palladium could be prepared even in water under basic conditions.[3] While continuing our efforts to synthesize sulfur ylide complexes of platinum, we have discovered a novel phase-transfer-catalyzed P–C bond cleavage reaction in Pt–dppm (dppm = $Ph_2PCH_2PPh_2$) complexes. Dppm has usually been used as a bridging ligand for binuclear or cluster complexes. Although it has been thought to be relatively inert under normal conditions, reports on the reaction of coordinated dppm have appeared.[4] The major reactions are deprotonation of the coordinated dppm and the reaction of the deprotonated dppm with electrophiles.[4] This paper reports the first example of the facile base hydrolysis of a dppm ligand in a Pt–dppm complex to a PPh_2Me and $PPh_2(OH)$ ligand. This phase-transfer-catalyzed reaction takes place under exceedingly mild conditions (room temperature, <2 N NaOH solution, normal PTC conditions).

Scheme I



Treatment of $Pt(dppm)Cl_2$ in CH_2Cl_2 with [$S(O)Me_3$]Cl in NaOH using n-Bu_4NCl as the phase-transfer catalyst gave a pale yellow compound, **1**,[5] in 85% yield. Other catalysts such as 15-crown-5 ether and n-$C_{16}H_{33}N(CH_3)_3Br$ work equally well. In the absence of a PT catalyst, results are varied, but normally the reaction is slow and side products are obtained. In this PT-catalyzed reaction, the dppm in the platinum compound was hydrolyzed, and a chelated sulfur ylide was formed. Addition of NH_4PF_6 to the ethanol solution of **1** gave a light yellow precipitate, **2**[6] (94% yield), which has PF_6 as a counteranion. The ^{31}P NMR spectrum of **1** indicates that there are two nonequivalent phosphorus atoms in a cis configuration—the upfield signal (2.4 ppm) is assigned to the coordinated PPh_2Me, while the downfield signal (51.5 ppm) is due to coordinated $PPh_2(OH)$. The ^1H NMR spectrum of **1** shows the presence of a coordinated PPh_2Me (δ = 1.89, 1:1:4:4:1:1 multiplet).[7] The position and relative intensity of the P–OH proton are less obvious due to the proton exchange between P–OH and H_2O present in the $CDCl_3$. The IR spectrum of **1** reveals the presence of an O–H stretching band at 3380 cm^{-1}. The molar conductance of **1** in acetone (15 Ω^{-1} cm^2 mol^{-1}) is lower than the values expected for a 1:1 electrolyte. Although compound **2** differs from **1** only

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[5] Compound 1: mp 157–159 °C; IR (KBr) ν(OH) 3380, ν(SO) 1180 cm^{-1}; Λ_M = 15 Ω^{-1} cm^2 mol^{-1}; ^1H NMR ($CDCl_3$) 7.2–7.7 (m), 3.09 (t, J(H,H) = 1.8 Hz), 2.1–2.4 (m), 1.89 (m, J(P,H) = 10 Hz, J(Pt,H) = 25.7 Hz) ppm; ^{31}P NMR ($CDCl_3$) 51.5 (m, J(P,P) = 24.4 Hz, J(Pt,P) = 3215.5 Hz), 2.4 (m, J(P,P) = 24.4 Hz, J(Pt,P) = 2948.5 Hz) ppm, downfield relative to 85% H_3PO_4. Anal. Calcd for $C_{28}H_{31}ClO_2P_2SPt$: C, 46.4; H, 4.3. Found: C, 46.3; H, 4.5.

[6] Compound 2: mp 120 °C (dec); IR (KBr) ν(OH) 3380, ν(SO) 1180 cm^{-1}; Λ_M = 67 Ω^{-1} cm^2 mol^{-1}; ^1H NMR ($CDCl_3$) 7.2–7.7 (m), 3.1 (t, J(H,H) = 1.8 Hz), 2.1–2.4 (m), 1.85 (m, J(P,H) = 10 Hz, J(Pt,H) = 25.7 Hz) ppm; ^{31}P NMR ($CDCl_3$) 67.9 (m, J(P,P) = 24.9 Hz, J(Pt,P) = 3245.1 Hz), 2.3 (m, J(P,P) = 24.9 Hz, J(Pt,P) = 2853.6 Hz), −143 (sept, J(P,F) = 706.2 Hz) ppm. Anal. Calcd for $C_{28}H_{31}F_6O_2P_3SPt$: C, 40.4; H, 3.7. Found: C, 40.2; H, 3.5.

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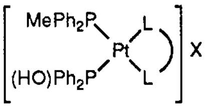
in its anion, 2 and 1 show large differences in phosphinous ^{31}P NMR chemical shift (16.4 ppm) and molar conductance (52 Ω^{-1} cm^2 mol^{-1}), suggesting that the chloride anion in 1 is probably associated with the cation through the acidic proton in P–OH. The interaction of a chloride anion with a coordinated P–OH proton has been reported.[8]



	L–L	X
1	$(CH_2)_2S(O)Me$	Cl
2	$(CH_2)_2S(O)Me$	PF_6
3	S_2CNEt_2	Cl
4	acetylacetonate	Cl

This phase-transfer catalyzed P–C bond cleavage of the dppm is general for other platinum complexes.[9] Treatment of $[Pt(dppm)(S_2CNEt_2)]Cl$ in CH_2Cl_2 with NaOH under PTC conditions gave the ionic compound 3[10] in 88% yield. Similarly, compound 4[11] can be formed in 60% yield from [Pt(dppm)(acac)]Cl (acac = acetylacetonate). On the other hand, this P–C bond cleavage is rather specific. Only dppm and not dppe (dppe = $Ph_2P(CH_2)_2PPh_2$) on the platinum is effective, and only one P–methylene bond on a Pt–dppm complex is broken.

While the formation of the Pt–sulfur ylide complex under PTC conditions can proceed in a way similar to the palladium analogy,[2] the hydrolysis of a dppm in Pt–dppm complexes to PPh_2Me and $PPh_2(OH)$ ligands under PTC/OH$^-$ is unknown. A similar but different reaction, the cleavage of a P–C bond in $Pt(dppm)Cl_2$ in liquid ammonia, has been reported.[12] In that reaction, a dppm ligand has been transformed to a methyldiphenylphosphine, PPh_2Me, and a diphenylphosphine oxide anion, PPh_2O^-. The latter is an anionic ligand instead of the neutral diphenylphosphinous acid (PPh_2OH) reported here. If our dppm cleavage products were identical with the known products of the dppm cleavage reaction, we should obtain neutral compounds instead of 1–4. In another reaction, photochemically induced dppm chelate ring expansion followed by hydrolysis has been reported to afford the $PPh_2(OH)$ ligand as one of the products.[13] The hydrolysis product, however, was obtained not by the direct hydrolysis of dppm but rather from an intermediate containing the six-membered chelate ring $\overline{\mathrm{MPOCCP}}$.

To demonstrate that this P–C bond hydrolysis does not have to go through deprotonation of dppm, we substituted the two methylene protons with two methyl groups and found that P–C bond hydrolysis also occurred although at slower rate. The probable pathway for the P–C bond cleavage in Pt–dppm complexes is shown in Scheme I. It is possible that the nucleophilic attack by OH$^-$ at one phosphorus followed by proton abstraction from water would produce the base-catalyzed hydrolysis products. We are currently investigating the factors that will influence the ease of this PT-catalyzed P–C bond hydrolysis and also ylide complex formation when using other sulfonium salts. Not only does this PT-catalyzed novel hydrolysis reaction suggest that dppm is not as stable as we used to think, but this is also a very easy way to convert a bidentate phosphine ligand to two different monodentate phosphines.

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Registry No. 1, 124399-74-2; 2, 124399-76-4; 3, 124399-77-5; 4, 124399-78-6; $Pt(dppm)Cl_2$, 52595-94-5; $[Pt(dppm)(S_2CNEt_2)]Cl$, 124417-99-8; [Pt(dppm)(acac)]Cl, 124418-00-4; $[S(O)Me_3]Cl$, 5034-06-0.

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(9) Base hydrolysis of $Pt(dppm)Cl_2$ also occurs under PTC/OH$^-$ conditions. However, more than two hydrolysis products have been observed.

(10) Compound **3**: mp 92–94 °C; IR (KBr) ν(OH) 3400 cm^{-1}; Λ_M = 24 Ω^{-1} cm^2 mol^{-1}; ^1H NMR ($CDCl_3$) 7.2–7.7 (m), 3.43 and 3.45 (q, J(H,H) = 7 Hz), 2.25 (m, J(P,H) = 11.2 Hz, J(Pt,H) = 40.3 Hz), 1.13 and 1.15 (t, J(H,H) = 7 Hz) ppm; ^{31}P NMR ($CDCl_3$) 41.1 (m, J(P,P) = 28.7 Hz, J(Pt,H) = 3322.3 Hz), 3.5 (m, J(P,P) = 28.7 Hz, J(Pt,H) = 3633.0 Hz). Anal. Calcd for $C_{30}H_{34}ClNOP_2S_2Pt$: C, 46.1; H, 4.4; N, 1.8. Found: C, 45.6; H, 4.6; N, 1.7.

(11) Compound **4**: mp 98–100 °C; IR (KBr) ν(OH) 3390 cm^{-1}; Λ_M = 9 Ω^{-1} cm^2 mol^{-1}; ^1H NMR ($CDCl_3$) 7.1–7.7 (m), 2.25 (s), 2.45 (m, J(P,H) = 12.0 Hz, J(Pt,H) = 45.0 Hz), 1.45 (s), 1.65 (s) ppm; ^{31}P NMR ($CDCl_3$) 23.8 (m, J(P,P) = 32.3 Hz, J(Pt,P) = 3647.5 Hz), 1.2 (m, J(P,P) = 32.3 Hz, J(Pt,P) = 4408.8 Hz). Anal. Calcd for $C_{30}H_{31}ClO_3P_2Pt$: C, 49.2; H, 4.2. Found: C, 49.4; H, 4.1.

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Iron Carbonyl Complexes of Isobenzofulvene

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Summary: Two stable iron carbonyl complexes of isobenzofulvene, a highly reactive molecule, are synthesized and characterized by ^1H NMR, ^{13}C NMR, IR, and MS spectroscopies.

We report the synthesis of the first transition-metal carbonyl complexes of isobenzofulvene (1). Isobenzofulvene (IBF) is a highly reactive cross-conjugated isomer of naphthalene that has proven to be unisolable under ordinary conditions.[1] The chemistry of IBF derivatives having substituents on the 1-, 3-, and/or 8-positions has been studied by Warrener,[2-7] Tanida,[8] Hafner,[9,10] and others.[11] Direct identification of 1 has only been achieved through the use of variable-temperature photoelectron spectroscopy (Scheme I). When the flash pyrolysis of 2 was carried out at 800 °C, 1 isomerized to naphthalene; even at very low temperatures, dimerization occurred to form 3.[12]

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