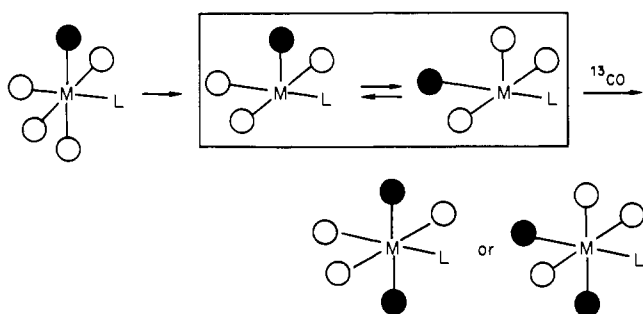
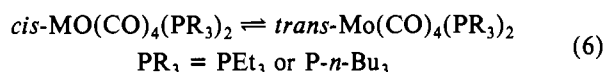


Scheme II



processes. For example, the importance of the electronic environment about the metal center is revealed in the non-dissociative ligand isomerization shown in eq 6 which readily



occurs with  $\Delta H^* = 24.5 \text{ kcal mol}^{-1}$ .<sup>31</sup> On the other hand, CO stereomobility in the  $\text{Mo(CO)}_5\text{PR}_3$  derivatives is apparently a more energetic process than ligand dissociation where  $E_a > 30 \text{ kcal mol}^{-1}$ .<sup>32</sup>

Thus far in our investigations of ligand stereomobility in  $\text{M(CO)}_5\text{L}$  derivatives by nondissociative routes we have observed this occurrence in chromium and tungsten complexes containing a number of phosphorus donor ligands, including those where  $\text{L} = \text{PPh}_3$ ,  $\text{PPh}_2\text{Me}$ , and  $\text{P(OMe)}_3$ . Although

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activation parameters have not as yet been determined for these rearrangements, it is apparent that  $\Delta H^*$  is less than that corresponding to ligand dissociation (i.e.,  $< 32 \text{ kcal mol}^{-1}$ ) and greater than  $16 \text{ kcal mol}^{-1}$ . This latter lower limit is suggested by the lack of line broadening in the  $^{13}\text{C}$  NMR of the carbonyl resonances in the high-temperature spectra of these derivatives.<sup>33</sup> More definitive assessments of activation parameters for ligand scrambling in  $\text{M(CO)}_5\text{PR}_3$  species ( $\text{M} = \text{Cr}$  or  $\text{W}$ ) are planned for future investigations.

A caveat which should be considered in CO-dissociative processes as described in Scheme II is that at least part of the ligand mobility often ascribed to rearrangement in the five-coordinate intermediates (boxed in Scheme II) produced may be due to intramolecular scrambling in the once formed six-coordinate product (see Scheme I). Further, in these processes where CO dissociation is *slow* relative to intramolecular ligand rearrangement in the six-coordinate species, no site preference for CO loss would be observable, although it would generally be anticipated on the basis of empirical as well as theoretical considerations.<sup>34</sup>

**Acknowledgment.** The financial support of this research by the National Science Foundation (Grant CHE 80-09233) is greatly appreciated.

**Registry No.** *trans*- $\text{Cr(CO)}_4(\text{PPh}_3)_2$ , 38800-75-8; *cis*- $\text{Cr(CO)}_4$ - $(^{13}\text{C})\text{PPh}_3$ , 81316-24-7;  $[\text{Et}_4\text{N}][\text{CO}_4(\text{PPh}_3)\text{Cl}]$ , 64654-62-2; CO, 630-08-0.

(33) In  $\text{M(CO)}_4(\text{EMe}_3)_2$  derivatives ( $\text{M} = \text{Fe, Ru, Os}$ ;  $\text{E} = \text{Si, Ge, Sn, Pb}$ )  $^{13}\text{C}$  NMR spectroscopy has been employed in establishing stereochemical nonrigidity in these six-coordinate complexes via a nondissociative process. Vancea, L.; Pomeroy, R. K.; Graham, W. A. *G. J. Am. Chem. Soc.* **1976**, *98*, 1407.

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## Notes

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### Rearrangement of Alkyl- and Arylsulfinato-S to Alkyl- and Arylsulfinato-O,O' Complexes of Platinum(II). Barrier to Desulfonylation

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The significant mechanistic steps for the desulfonylation of arylsulfonfyl halides by noble-metal complexes<sup>1</sup> include the attachment of the arylsulfonfyl moiety on the transition-metal atom by substitution or oxidative-addition reactions, the rearrangement (migration) of the aryl group from sulfur dioxide to the metal atom, and the subsequent expulsion of the sulfur dioxide molecule. Only few examples of stoichiometric desulfonylation have been reported.<sup>2</sup> Attempts to induce elimination of sulfur dioxide from alkyl- or arylsulfinato complexes by creation of vacant coordination sites on the metal atom by photochemical or thermal extrusion schemes have been generally futile.<sup>2a,b</sup> Desulfonylation of *trans*- $[\text{PtL}_2(\text{RSO}_2)\text{Cl}]$  (where L is  $\text{PPh}_3$ <sup>3</sup> or  $\text{PMe}_2\text{Ph}$ <sup>4</sup> and R is *p*-tolyl) proceeds only

at high temperature. It has been suggested that the vacant metal site on four-coordinate Pt(II) may provide a suitable pathway for alkyl or aryl migration and subsequent desulfonylation.<sup>2</sup> However,  $[\text{Pt}(\text{PEt}_3)_2\text{Cl}(p\text{-tol-SO}_2)]$  cannot be desulfonylated.<sup>4</sup> We have also observed that thermal desulfonylation is not facile for (alkylsulfinato)platinum(II) complexes. The difficulty of extrusion of  $\text{SO}_2$  from transition-metal sulfonates has been attributed at least in part to the strength of the metal-sulfur bond.<sup>2b</sup> Since silver ion abstraction of chloride from the acyl complexes  $[\text{Pt}(\text{PPh}_3)_2(\text{RCO})\text{Cl}]$  promotes facile alkyl and aryl migration from CO to Pt,<sup>5</sup> it was of interest to determine if similar chloride abstraction from sulfonate complexes  $[\text{Pt}(\text{PPh}_3)_2(\text{RSO}_2)\text{Cl}]$  would lead to alkyl- and arylplatinum complexes.

### Experimental Section

Alkyl- and arylsulfonfyl chlorides were distilled or sublimed before use. Benzene was distilled from  $\text{P}_2\text{O}_5$  and stored over molecular sieves.  $\text{Pt}(\text{PPh}_3)_4$  and  $[\text{Pt}(\text{PPh}_3)_2\text{C}_2\text{H}_4]$  were prepared by the usual methods.<sup>6,7</sup> All other chemicals were reagent grade metals, which were used without further treatment. The platinum(0) complexes were manipulated under a nitrogen atmosphere with use of Schlenk tubes. Microanalyses were performed by Chemalytics, Inc., Tempe, AZ. Infrared spectra were recorded in Nujol mulls on a Perkin-Elmer 621 spectrophotometer. Proton magnetic resonance spectra were obtained with a Varian EM-360 spectrometer, and shifts were obtained relative

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Table I. Analytical and IR Spectral Data (cm<sup>-1</sup>)

complex	mp °C (dec), <sup>b</sup>	anal. found (calcd)			$\nu_a(\text{SO}_2)$	$\nu_s(\text{SO}_2)$	$\nu(\text{Pt-Cl})$
		% C	% H	% Cl			
[Pt(PPh <sub>3</sub> ) <sub>2</sub> Cl(CH <sub>3</sub> SO <sub>2</sub> )]	208	53.5 (53.3)	4.05 (3.99)		1210	1065	309
[Pt(PPh <sub>3</sub> ) <sub>2</sub> Cl(C <sub>2</sub> H <sub>5</sub> SO <sub>2</sub> )]	245	53.1 (53.8)	3.88 (4.16)		1200	1060	307
[Pt(PPh <sub>3</sub> ) <sub>2</sub> Cl(C <sub>3</sub> H <sub>7</sub> SO <sub>2</sub> )]	207	53.3 (54.3)	4.15 (4.32)	4.34 (4.11)	1192	1063	313
[Pt(PPh <sub>3</sub> ) <sub>2</sub> Cl(C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> )] <sup>a</sup>	190	53.0 (52.6)	3.89 (3.80)	10.9 (10.8)	1206	1054	312
[Pt(PPh <sub>3</sub> ) <sub>2</sub> Cl( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> )] <sup>c</sup>	127	54.7 (54.2)	3.95 (3.68)	7.81 (7.62)	1215	1053	314
[Pt(PPh <sub>3</sub> ) <sub>2</sub> Cl( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> )]	130	56.8 (56.7)	4.67 (4.10)		1208	1046	311
[Pt(PPh <sub>3</sub> ) <sub>2</sub> Cl( <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> )] <sup>a</sup>	206	52.3 (52.3)	3.97 (3.89)	11.1 (10.5)	1202	1046	310
[Pt(PPh <sub>3</sub> ) <sub>2</sub> Cl( <i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> )]	120	54.4 (53.6)	3.58 (3.64)	1.87 (1.49) <sup>d</sup>	1204	1058	310
[Pt(PPh <sub>3</sub> ) <sub>2</sub> (CH <sub>3</sub> SO <sub>2</sub> )]PF <sub>6</sub> <sup>f,g</sup>	144	46.1 (47.1)	3.61 (3.53)	3.20 (3.40) <sup>e</sup>	1190	950	
[Pt(PPh <sub>3</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> SO <sub>2</sub> )]PF <sub>6</sub> <sup>f,g</sup>	126	48.2 (48.2)	3.62 (3.84)	4.54 (3.30) <sup>e</sup>	1190	940	
[Pt(PMe <sub>2</sub> Ph) <sub>2</sub> (CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> )]PF <sub>6</sub> <sup>f</sup>	113	35.7 (35.8)	3.95 (3.79)	3.96 (4.16) <sup>e</sup>	1190	910	
[Pt(PPh <sub>3</sub> ) <sub>2</sub> (CH <sub>3</sub> CN)(CH <sub>3</sub> SO <sub>2</sub> )]PF <sub>6</sub> <sup>f,g</sup>	175	47.1 (47.6)	3.99 (3.68)	1.22 (1.42)	1220	1073	
[Pt(PPh <sub>3</sub> ) <sub>2</sub> (CH <sub>3</sub> CN)( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> )]PF <sub>6</sub> <sup>f,g</sup>	154	47.7 (48.9)	3.26 (3.45)	1.09 (1.29)	1231	1067	
[Pt(PPh <sub>3</sub> ) <sub>2</sub> (CH <sub>3</sub> CN)( <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> )]PF <sub>6</sub> <sup>f,g</sup>	118	48.1 (47.6)	3.82 (3.64)	1.31 (1.21)	1221	1067	

<sup>a</sup> Solvated by CH<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup> Decomposition starts. <sup>c</sup> Analysis for S: 3.18 (3.44). <sup>d</sup> Analysis for N. <sup>e</sup> Analysis for S. <sup>f</sup>  $\nu(\text{PF}_6)$  at 834 cm<sup>-1</sup>. <sup>g</sup> Additional absorption at 550 cm<sup>-1</sup> (s).

to internal Me<sub>4</sub>Si. Conductivities were measured with a YSI Model 31 bridge.

#### Chloro(alkylsulfinato)bis(triphenylphosphine)platinum(II). Method

**A.** A solution of 0.95 mL (1.21 mmol) of methanesulfonyl chloride in 5-mL of benzene was added rapidly to a solution of 1.50 g (1.21 mmol) of (Ph<sub>3</sub>P)<sub>4</sub>Pt in 30 mL of benzene. After 3–5 s of stirring, the resulting solution was immediately quenched with 60 mL of hexane to precipitate a very pale yellow solid. The product was washed with diethyl ether and recrystallized from dichloromethane/diethyl ether. The other sulfinato complexes shown in Table I were prepared in a similar manner.

**Method B.** Pt(PPh<sub>3</sub>)<sub>2</sub>C<sub>2</sub>H<sub>4</sub> (300 mg, 0.40 mmol) was dissolved in 10 mL of benzene, and 0.1 mL of *n*-C<sub>3</sub>H<sub>7</sub>SO<sub>2</sub>Cl (1 mmol) was added. After 30 s of stirring, the color of the yellow solution faded, and 15 mL of diethyl ether was added to precipitate the pale yellow (nearly colorless) solid, which was washed with 20 mL of Et<sub>2</sub>O and dried in vacuo; yield 320 mg (93%). The other sulfinato complexes were also prepared in a similar manner.

**Method C.** A mixture of 473 mg (0.87 mmol) of [Pt(PMe<sub>2</sub>Ph)<sub>2</sub>Cl<sub>2</sub>] in 40 mL of dichloromethane and 224 mg (1.26 mmol) of NaCH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub> and 50 mg of Me<sub>4</sub>NCl (phase-transfer catalyst) in 30 mL of water was stirred for 6 h. The dichloromethane layer was separated from the aqueous phase. The solvent was evaporated in vacuo, and the product was washed with water, ethanol, and ether. The product was recrystallized from dichloromethane/ether; yield 520 mg (90%).

**Reaction of Chloro(alkylsulfinato)bis(triphenylphosphine)platinum(II) with AgPF<sub>6</sub>.** A 100-mg (0.12-mmol) quantity of chloro-(methylsulfinato)bis(triphenylphosphine)platinum(II) and 31 mg (0.12 mmol) of silver hexafluorophosphate were stirred in 5 mL of dichloromethane for 5 min. The resulting suspension was centrifuged, and the silver chloride resulting from the reaction was removed by filtration. The filtrate was reduced in volume to 1.5 mL under reduced pressure and diethyl ether added to precipitate a white solid. The product was recrystallized from dichloromethane/diethyl ether. Rearrangements of other sulfinato complexes were effected in a similar manner.

**(Alkylsulfinato)(acetonitrile)bis(triphenylphosphine)platinum(II) Hexafluorophosphate.** A 100-mg (0.12-mmol) quantity of chloro-(methylsulfinato)bis(triphenylphosphine)platinum(II) and 31 mg (0.12 mmol) of silver hexafluorophosphate were stirred in 5 mL of acetonitrile for 5 min. The resulting suspension was centrifuged, and the silver chloride was removed by filtration. The filtrate was reduced in volume to 1.5 mL under reduced pressure and diethyl ether added to precipitate a white solid. The product was recrystallized from acetonitrile/diethyl ether. Other sulfinato-acetonitrile complexes were prepared in a similar manner.

#### Results and Discussion

The synthesis of the alkyl- and arylsulfinato complexes [Pt(PPh<sub>3</sub>)<sub>2</sub>(R'SO<sub>2</sub>)Cl] (I) by the previous published method of oxidative addition<sup>3</sup> of R'SO<sub>2</sub>Cl to [Pt(PPh<sub>3</sub>)<sub>4</sub>] was found not to be generally successful. Mixtures of substances with IR spectra that had low absorption intensities in the S–O stretching region (1210–1060 cm<sup>-1</sup>) were obtained. The

sulfinato complexes I could be obtained in yields of 75–95% only by rapidly precipitating the product with hexane immediately after mixing stoichiometric quantities of the reactants in benzene. The complications in the reaction arise from the subsequent reactions of products from the complex reaction of triphenylphosphine and alkyl- and arylsulfonyl chlorides.<sup>8</sup> A convenient and reproducible synthesis of the sulfinato complexes (I) was the reaction of sulfonyl chlorides with [Pt(PPh<sub>3</sub>)<sub>2</sub>C<sub>2</sub>H<sub>4</sub>].<sup>9</sup> The phase-transfer-catalyzed reaction of [Pt(PMe<sub>2</sub>Ph)Cl<sub>2</sub>] and NaRSO<sub>2</sub> was found to be a convenient method for the synthesis of the sulfinato complexes.

The sulfinato complexes shown in Table I have  $\nu_a(\text{S-O})$  vibrations in the 1190–1220 cm<sup>-1</sup> region and  $\nu_s(\text{S-O})$  in the 1040–1065 cm<sup>-1</sup> region, which are characteristic of sulfinato-S complexes.<sup>2</sup> The trans structure for the sulfinato-S complexes is indicated by infrared data: the absence of the intense band at 550 ± 5 cm<sup>-1</sup>, which is observed in the IR spectra of *cis*-bis(organophosphine)platinum(II) complexes.<sup>10</sup> The correlation has been repeatedly confirmed by <sup>31</sup>P and <sup>1</sup>H NMR data.<sup>11</sup> The trans structure of [Pt(PMe<sub>2</sub>Ph)<sub>2</sub>(CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>)Cl] has also been shown by proton magnetic resonance data.<sup>4</sup> The reaction of AgPF<sub>6</sub> with [Pt(PPh<sub>3</sub>)<sub>2</sub>Cl(RSO<sub>2</sub>)] (R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, *n*-C<sub>3</sub>H<sub>7</sub>, C<sub>6</sub>H<sub>5</sub>, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>) in dichloromethane gave silver chloride and complexes that do not have the very intense IR absorption bands in the 1210- and 1060-cm<sup>-1</sup> regions that are characteristic of the sulfinato-S complexes (Table I). The compounds [Pt(PPh<sub>3</sub>)<sub>2</sub>(RSO<sub>2</sub>)]PF<sub>6</sub> have IR absorption bands in the 910–965 cm<sup>-1</sup> region, which is characteristic of the bidentate sulfinato-*O,O'* complexes.<sup>2c,12</sup> These compounds have the very intense band at 835 cm<sup>-1</sup> due to the PF<sub>6</sub> anion. The measured molar conductance of [Pt(PMe<sub>2</sub>Ph)<sub>2</sub>(SO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)]PF<sub>6</sub> in nitromethane (60 cm<sup>2</sup>/Ω mol) compares favorably with the value 63 cm<sup>2</sup>/Ω mol found for the 1:1 electrolyte [Pt(PPh<sub>3</sub>)<sub>2</sub>ClCO]BF<sub>4</sub>.

That the abstraction of chloride leads to formation of *cis* complexes is supported by the proton magnetic resonance spectrum of [Pt(PMe<sub>2</sub>Ph)<sub>2</sub>(CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>)]PF<sub>6</sub>, which has a complex multiplet centered at 1.67 ppm (12 H) and a singlet at 2.40 ppm (3 H) compared to the spectrum of *trans*-[Pt(PMe<sub>2</sub>Ph)<sub>2</sub>Cl(C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>SO<sub>2</sub>)], which has three triplets centered at 1.45 ppm (12 H) and a singlet at 2.12 ppm (3 H). Addition of sodium chloride to [Pt(PMe<sub>2</sub>Ph)<sub>2</sub>-

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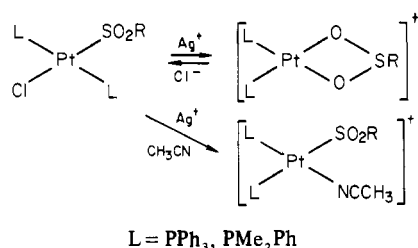
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Scheme I



(CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>)]PF<sub>6</sub> gave the original sulfinato-S complex [Pt(PMe<sub>2</sub>Ph)<sub>2</sub>(CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>)Cl].

The addition of AgPF<sub>6</sub> in acetonitrile to the sulfinato complexes did not give the rearranged sulfinato-O,O' complexes but instead gave the complexes [Pt(PPh<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>CN)(SO<sub>2</sub>R)]PF<sub>6</sub>, which have intense sulfinato S=O absorption in the 1230- and 1060-cm<sup>-1</sup> regions (see Table I) and nitrile C≡N absorption in the 2300-2310 cm<sup>-1</sup> region. These compounds also have the very intense PF<sub>6</sub> absorption centered at 840 cm<sup>-1</sup>.

The products of reactions conducted in this study are summarized in Scheme I. In contrast to the facile migration of alkyl or aryl R' groups from CO to Pt upon treatment of [Pt(PR<sub>3</sub>)<sub>2</sub>Cl(R'CO)] with silver ion,<sup>5</sup> the reaction of [Pt(PR<sub>3</sub>)<sub>2</sub>Cl(R'SO<sub>2</sub>)] with silver ion does not lead to migration of R' from SO<sub>2</sub> to Pt but rather to rearrangement of the sulfinato-S to the sulfinato-O,O' complex. The difficulty of elimination of SO<sub>2</sub> from sulfinato complexes and a significant barrier to desulfonylation may thus be attributed to the possible rearrangement of the sulfinato-S to the sulfinato-O,O' complex, which will utilize vacant coordination sites needed for alkyl or aryl migration.

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**Registry No.** Pt(PPh<sub>3</sub>)<sub>2</sub>Cl(CH<sub>3</sub>SO<sub>2</sub>), 57692-69-0; Pt(PPh<sub>3</sub>)<sub>2</sub>Cl(C<sub>2</sub>H<sub>5</sub>SO<sub>2</sub>), 80975-57-1; Pt(PPh<sub>3</sub>)<sub>2</sub>Cl(C<sub>3</sub>H<sub>7</sub>SO<sub>2</sub>), 80964-52-9; Pt(PPh<sub>3</sub>)<sub>2</sub>Cl(C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>), 57692-70-3; Pt(PPh<sub>3</sub>)<sub>2</sub>Cl(*p*-ClC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>), 80975-56-0; Pt(PPh<sub>3</sub>)<sub>2</sub>Cl(*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>), 80964-51-8; Pt(PPh<sub>3</sub>)<sub>2</sub>Cl(*p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>), 80964-50-7; Pt(PPh<sub>3</sub>)<sub>2</sub>Cl(*p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>), 80964-49-4; [Pt(PPh<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>SO<sub>2</sub>)]PF<sub>6</sub>, 80964-57-4; [Pt(PPh<sub>3</sub>)<sub>2</sub>(C<sub>3</sub>H<sub>7</sub>SO<sub>2</sub>)]PF<sub>6</sub>, 80964-59-6; [Pt(PMe<sub>2</sub>Ph)<sub>2</sub>(CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>)]PF<sub>6</sub>, 80964-61-0; [Pt(PPh<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>CN)(CH<sub>3</sub>SO<sub>2</sub>)]PF<sub>6</sub>, 80964-48-3; [Pt(PPh<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>CN)(*p*-ClC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>)]PF<sub>6</sub>, 80975-55-9; [Pt(PPh<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>CN)(*p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>)]PF<sub>6</sub>, 80964-46-1; Pt(PMe<sub>2</sub>Ph)<sub>2</sub>Cl<sub>2</sub>, 38928-82-4; (Ph<sub>3</sub>P)<sub>4</sub>Pt, 14221-02-4; Pt(PPh<sub>3</sub>)<sub>2</sub>C<sub>2</sub>H<sub>4</sub>, 12120-15-9.

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### Cyclometalation of Arylazo Compounds. 3.<sup>1</sup> Determination of the Chelate Ring Size in a Peri-Palladated 1-Arylazonaphthalene by Nitrogen-15 Nuclear Magnetic Resonance

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Our interest in regiospecific cyclopalladation has been stated before.<sup>1,3</sup> By altering substituents in the arylazonaphthalene

ligand, the site of metalation at either of the three ortho positions could partially be governed. Cyclopalladation at the peri position in the naphthyl moiety was achieved only after all the ortho positions had been substituted by methyl groups. Thus, the azo ligand 3 reacted with Na<sub>2</sub>PdCl<sub>4</sub> to complex 4 with a Pd-arene σ bond at carbon atom C(8), as was confirmed by <sup>1</sup>H NMR<sup>1</sup> and by cleaving the Pd-C bond with NaBD<sub>4</sub>.<sup>2</sup> No decision could be made, however, as to which of the azo nitrogen atoms had been coordinated: closure of the chelate ring at N<sub>α</sub><sup>4</sup> would result in a five-membered ring structure, whereas cyclopalladation at N<sub>β</sub><sup>4</sup> would lead to a six-membered chelate.

According to Cope and Friedrich,<sup>5</sup> the formation of a five-membered chelate seems to be a necessary prerequisite for cyclopalladation to occur. This has been corroborated by numerous cyclopalladated complexes,<sup>6-8</sup> and to our knowledge only three examples of six-membered Pd chelates with Pd-C σ bonds have been reported in the literature.<sup>9,10,20</sup> In other cases, an intermediate formation of a six-membered palladacycle in a Pd(II)-catalyzed reaction can be postulated.<sup>11,12</sup>

<sup>15</sup>N NMR spectroscopy has proved to be a promising method for distinguishing between the two possible structures of complex 4: as bonding to a nitrogen lone pair (by a proton<sup>13</sup> or by a metal center<sup>14</sup>) causes dramatic changes in <sup>15</sup>N chemical shifts, <sup>15</sup>N labeling of either N<sub>α</sub> or N<sub>β</sub> and comparing the <sup>15</sup>N resonances of the ligands with those of the palladated complexes would offer conclusive proof of the chelate ring size.

### Experimental Section

**<sup>15</sup>N NMR Spectra.** Ligands and complexes were measured as 2% (CH<sub>3</sub>)<sub>2</sub>SO<sup>15</sup> solutions on a Bruker WM-250 spectrometer<sup>16</sup> operating at 25.33 MHz in the FT mode. <sup>15</sup>N chemical shifts are related to formamide as external reference (112.4 ppm with respect to 0 ppm for anhydrous liquid ammonia at 25 °C<sup>17</sup>).

<sup>15</sup>N-labeled ligands 1 (<sup>15</sup>N<sub>β</sub>) and 3 (<sup>15</sup>N<sub>β</sub>) and Pd(II) complexes 2 (<sup>15</sup>N<sub>β</sub>) and 4 (<sup>15</sup>N<sub>β</sub>) were synthesized in the same way as their unlabeled analogues.<sup>1</sup> The <sup>15</sup>N<sub>β</sub> label was introduced by diazotization of 1-aminonaphthalene with Na<sup>15</sup>NO<sub>2</sub> (Stohler Isotope Chemicals, 99% <sup>15</sup>N). For the <sup>15</sup>N<sub>α</sub>-labeled azo ligand 3 (<sup>15</sup>N<sub>α</sub>), a partially different method was applied: 1-[<sup>15</sup>N]amino-2-methylnaphthalene was synthesized by nitration of 2-methylnaphthalene<sup>18</sup> with H<sup>15</sup>NO<sub>3</sub> (60.2% solution, Stohler Isotope Chemicals, 99% <sup>15</sup>N) and Béchamp reduction of the resulting nitro compound.<sup>19</sup> Diazotization of 1-

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