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Intermediates in the Reaction of *trans*-$Cr(CO)_4(PPh_3)_2$ with ^{13}CO and Fluxionality in Octahedral Group 6B Metal Carbonyls via a Nondissociative Mechanism

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The stereoselectivity of the dissociative process involving the reaction of *trans*-$Cr(CO)_4(PPh_3)_2$ with ^{13}C-labeled carbon monoxide to afford the pentacarbonylchromium triphenylphosphine derivative is examined. The data presented are consistent with a completely stereoselective process where the incoming ^{13}CO ligand occupies a site in the octahedral complex cis to the PPh_3 ligand (i.e., formation of *cis*-$Cr(CO)_4(^{13}CO)PPh_3$). Hence rearrangement of the initially formed $[Cr(CO)_4PPh_3]$ intermediate of C_{4v} symmetry to that of C_s symmetry occurs faster than the bimolecular reaction of the intermediate with carbon monoxide. A subsequent reaction involving a stereomobility of the ligands in the six-coordinate derivative is observed which takes place in the absence of ligand (CO or PPh_3) dissociation. Comparisons with the analogous processes involving the molybdenum derivatives are presented. Similar ligand stereomobility in other phosphine or phosphite complexes of chromium and tungsten are summarized.

Introduction

The initial step in many ligand replacement reactions in organometallic chemistry involves dissociation of the leaving ligand from a coordinatively saturated metal complex. In the nomenclature of Langford and Gray[3] this dissociative pathway, which affords an intermediate of reduced coordination number, is designated D (eq 1). During the past few years several

$$ML_n \underset{+L}{\overset{-L}{\rightleftharpoons}} ML_{n-1} \underset{-L'}{\overset{+L'}{\rightleftharpoons}} ML_{n-1}L' \qquad (1)$$

studies have been done in an attempt to correlate the rate of ligand dissociation with the steric size or binding strength of L in $M(CO)_{6-n}L_n$ derivatives, where M = group 6B metal.[4] Current attention has focused on a discussion of the solution structure and reactivity of the five-coordinate $[M(CO)_{5-n}L_n]$ transients provided during these processes.[5-10]

Wovkulich, Feinberg, and Atwood have recently published a kinetic study of the reaction of a variety of *trans*-$Cr(CO)_4L_2$ species with CO (eq 2), where L = $P(C_4H_9)_3$, $P(OC_6H_5)_3$,

$$trans\text{-}Cr(CO)_4L_2 + CO \rightarrow Cr(CO)_5L + L \qquad (2)$$

$P(OCH_3)_3$, $P(C_6H_5)_3$, and $As(C_6H_5)_3$).[4e] These researchers assumed the intermediates in these processes, $[Cr(CO)_4L]$, to be similar in character to the molybdenum analogues, $[Mo(CO)_4L]$, which we have reported upon previously.[4d] In order to unequivocally establish the generality of the behavior of five-coordinate intermediates of the group 6B metal triad, we have examined reaction 2 employing ^{13}C-labeled carbon monoxide. An adventitious phenomenon of consequence in this report, which was not present in the molybdenum system, is the propensity of six-coordinate chromium carbonyl derivatives to undergo ligand rearrangements via a nondissociative process.[11,12]

Experimental Section

Materials. Tetrachloroethylene was Spectro Grade solvent obtained from Matheson Coleman and Bell. ^{13}CO gas enriched to >90% was acquired from Prochem, BOC Ltd., London.

Synthesis. $Cr(CO)_5PPh_3$ and *trans*-$Cr(CO)_4(PPh_3)_2$ were prepared according to the literature procedure.[13] $[Et_4N][Cr(CO)_4(PPh_3)Cl]$ was synthesizd by the irradiation of *trans*-$Cr(CO)_4(PPh_3)_2$ in the presence of halide ion.[14]

***cis*-$Cr(CO)_4(^{13}CO)PPh_3$.** Approximately 25 mL of EtOH was placed in a 50-mL Schlenk flask, cooled to −50 °C, and saturated with ^{13}CO. A 0.5-g sample of $[Et_4N][Cr(CO)_4(PPh_3)Cl]$ was added to the flask, and the solution was kept at −50 °C for 10 min and then slowly allowed to warm up to ambient temperature. After 30 min of stirring at room temperature, the solution was filtered under nitrogen and the solvent removed under reduced pressure to yield the light yellow product. The infrared spectrum of the product in hexane in the ν(CO) region exhibited bands at 2057, 1977, 1942, and 1912 cm^{-1}. The cis ⇌ trans isomerization of the stereoselectively ^{13}CO-labeled complex was effected by stirring the complex in a tetrachloroethylene solution at 40 °C.

Reaction of *trans*-$Cr(CO)_4(PPh_3)_2$. A 1.08-g sample of *trans*-$Cr(CO)_4(PPh_3)_2$ was placed in a 100-mL Schlenk flask in 40 mL of tetrachloroethylene, and the mixture was stirred under a ^{13}CO atmosphere at 55 °C. Samples were withdrawn periodically, and the progress of the reaction was monitored by infrared and ^{13}C NMR spectroscopy.

Infrared Measurements. The infrared spectra were recorded in 1.0-mm matched NaCl sealed cells on a Perkin-Elmer 283B spectrophotometer equipped with an Infrared Data Station and employing the PECDS software package provided by Perkin-Elmer. The spectra were calibrated against a water-vapor spectrum below 2000 cm^{-1} and against a CO spectrum above 2000 cm^{-1}.

^{13}C NMR Measurements. The ^{13}C NMR spectra were recorded on a JEOL FX60 spectrometer operated at 15.03 MHz with an internal deuterium lock. Samples were run in $CDCl_3$ solvent at ambient temperature in 10-mm tubes. Spectra were determined employing a sweep width of 4000 Hz (16K data block) with an acquisition time of 2 s, a pulse repetition rate of 5 s, and a flip angle of 30°.

Results and Discussion

The activation parameters determined for the reaction described in eq 2 for L = PPh_3 ($\Delta H^* = 31.3 \pm 1.2$ kcal mol^{-1} and $\Delta S^* = 21.2 \pm 3.6$ eu)[15] are indicative of a process involving dissociative loss of L from $Cr(CO)_4L_2$ in the rate-

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(1) Tulane University.
(2) Universität Würzburg.
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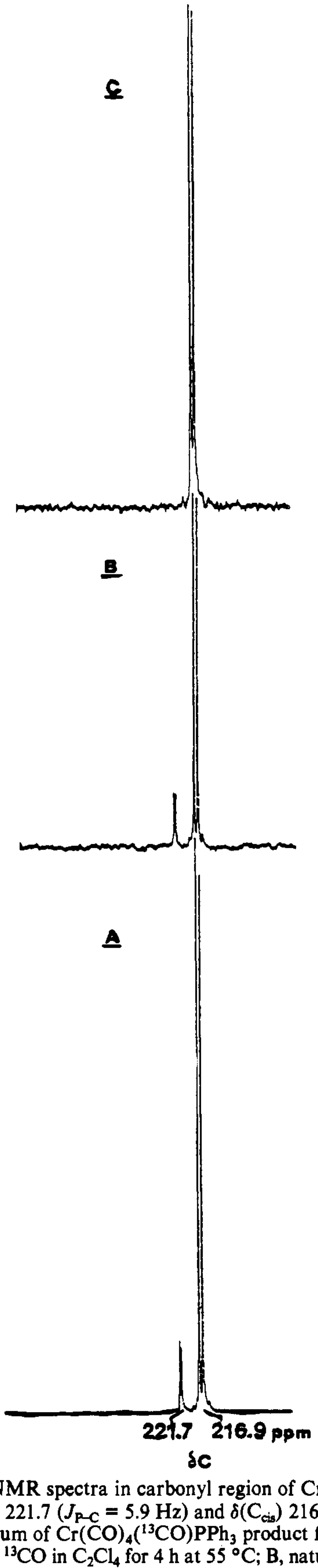

Figure 1. ^{13}C NMR spectra in carbonyl region of $Cr(CO)_5PPh_3$ in $CDCl_3$ [$\delta(C_{trans})$ 221.7 (J_{P-C} = 5.9 Hz) and $\delta(C_{cis})$ 216.9 (J_{P-C} = 13.0 Hz)]: A, spectrum of $Cr(CO)_4(^{13}CO)PPh_3$ product from *trans*-$Cr(CO)_4(PPh_3)_2$ + ^{13}CO in C_2Cl_4 for 4 h at 55 °C; B, natural-abundance spectrum; C, spectrum of *cis*-$Cr(CO)_4(^{13}CO)PPh_3$ prepared from *cis*-$Cr(CO)_4(PPh_3)Cl^-$ + ^{13}CO.

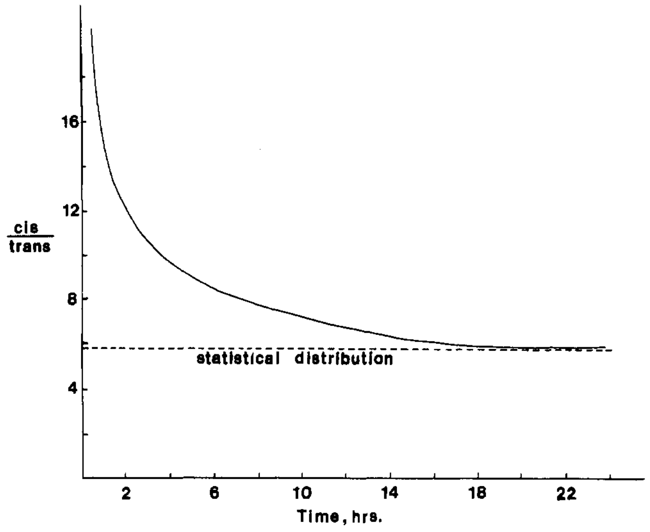

Figure 2. Variation in intensity ratio of $\delta(C_{eq})/\delta(C_{ax})$ absorptions in $Cr(CO)_5PPh_3$ as *cis*-$Cr(CO)_4(^{13}CO)PPh_3$ isomerizes to the equilibrium distribution of *cis*- and *trans*-$Cr(CO)_4(^{13}CO)(PPh_3)$ at 40 °C in C_2Cl_4.

determining step with concomitant formation of $[Cr(CO)_4L]$.[4c] Since the disposition of the L ligands are mutually trans in the starting material, the geometry of the primary intermediate is expected to be square pyramidal with the unique ligand (L) occupying the axial coordination site (C_{4v} symmetry). Bimolecular rate constants for reactions of the $[Cr(CO)_5]$ intermediate with a variety of incoming ligands are in the range 10^7–10^8 M^{-1} s^{-1}; hence trapping experiments of the $[Cr(CO)_4L]$ (C_{4v}) species with ^{13}CO should be informative in establishing its solution stability.[10,16]

Figure 1A depicts the ^{13}C NMR spectrum in the carbonyl region for the $Cr(CO)_4(^{13}CO)PPh_3$ product derived from eq 3. Comparison of this ^{13}C NMR spectral result with that

$$trans\text{-}Cr(CO)_4(PPh_3)_2 + {}^{13}CO \rightarrow Cr(CO)_4({}^{13}CO)PPh_3 \quad (3)$$

obtained on a natural-abundance sample of $Cr(CO)_5PPh_3$ (Figure 1B) demonstrated reaction 3 to be stereoselective in production of the *cis*-$Cr(CO)_4(^{13}CO)PPh_3$ species. Similar experiments, where reaction 3 was quenched at various time intervals and examined by ^{13}C NMR, clearly indicated that the degree of stereoselectivity of cis ^{13}CO labeling in the product species decreased with reaction time. Since both *trans*-$Cr(CO)_4(PPh_3)_2$ and $Cr(CO)_5PPh_3$ were found to be completely inert toward CO substitution under these mild reaction conditions, this observation dictates subsequent ligand rearrangements to be occurring in the product molecule by a nondissociative pathway.[11,12] Indeed, control experiments employing stereoselectively ^{13}CO-labeled *cis*-$Cr(CO)_4(^{13}CO)PPh_3$ derivative (see Figure 1C), prepared by means of reaction 4, showed that ligand rearrangement in this species

$$cis\text{-}Cr(CO)_4(PPh_3)Cl^- + {}^{13}CO \xrightarrow[-50\ °C]{EtOH} cis\text{-}Cr(CO)_4({}^{13}CO)PPh_3 + Cl^- \quad (4)$$

occurs via a nondissociative process on a time scale similar to that of PPh_3 dissociation in *trans*-$Cr(CO)_4(PPh_3)_2$. Specifically, the rate constant for PPh_3 dissociation from *trans*-$Cr(CO)_4(PPh_3)_2$ in dichloroethane has been determined by Atwood and Wovkulich[15] to be 4.15×10^{-5} s^{-1} at 40 °C. Figure 2 illustrates the variation of the intensity ratio of $\delta(C_{eq})/\delta(C_{ax})$ with reaction time as eq 5 approaches equilibrium. An in-

$$cis\text{-}Cr(CO)_4({}^{13}CO)PPh_3 \rightleftharpoons trans\text{-}Cr(CO)_4({}^{13}CO)PPh_3 \quad (5)$$

tensity ratio of 5.8 was observed in the natural-abundance $Cr(CO)_5PPh_3$ sample (see Figure 1B). A value of the rate constant for CO scrambling in the six-coordinate $Cr(CO)_5PPh_3$

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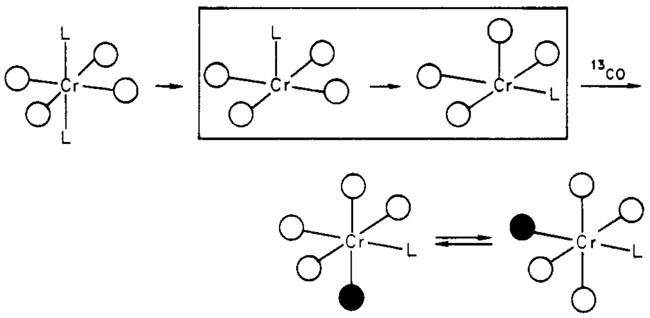
Scheme I



species of 3.13×10^{-5} s^{-1} at 40 °C in C_2Cl_4 has been measured. Unfortunately, the ^{13}C NMR method for determining the rate constant for nondissociative rearrangement involves a sizable error (perhaps as high as ± 20%). Within the error limits of the rate data, these observations are consistent with complete stereoselectivity in the formation of the *cis*-$Cr(CO)_4(^{13}CO)PPh_3$ via reaction 3, with rearrangement to a statistically scrambled ^{13}CO ligand occurring in a subsequent process by a nondissociative mechanism. The lack of ^{13}CO incorporation into $Cr(CO)_5PPh_3$ as well as $Cr(CO)_5(^{13}CO)$ formation, in a control experiment carried out between $Cr(CO)_5PPh_3$ and ^{13}CO under the reaction conditions of eq 3 further substantiate the nondissociative nature of the stereomobility of the CO ligands in the pentacarbonyl derivative. Indeed, these ligand substitution reactions require considerably more drastic reaction conditions than those employed in this study. For example, the rate constant for CO dissociation in $Cr(CO)_5PPh_3$ is 3×10^{-10} s^{-1} at 30 °C,[5] whereas, the corresponding parameter for phosphine dissociation is 9.97×10^{-5} at 130 °C.[4f]

The ^{13}C NMR spectrum of $Cr(CO)_5PPh_3$ observed in toluene-d_8 at 80 °C, where dissociative CO loss is slow, exhibited no broadening of the axial and equatorial CO resonances ($\Delta\nu$ = 68.6 Hz at 23 °C) (see Figure 3). This would be anticipated for an intramolecular scrambling process which has a rate constant of only 3.13×10^{-5} s^{-1} at 40 °C, i.e., an increase in temperature of 40 °C, would not be expected to increase this rate constant to where it would approach k_{coalesc} (approximately $2.22(\Delta\nu)$).[17] On the other hand, we observed stereomobility on the NMR time scale for the CO ligand in $HCr(CO)_5^-$ where a coalescence temperature of ~−6 °C has been determined.[18,19]

Hence, these experiments indicate that the five-coordinate, $[Cr(CO)_4PPh_3]$, intermediate afforded in reaction 2 rearranges to incorporate CO cis to the phosphine ligand (Scheme I).[20] This in turn necessitates that the $C_{4v} \rightarrow C_s$ intramolecular rearrangement occurs with a rate constant greater than 3×10^4 s^{-1} with the assumption that $[Cr(CO)_4PPh_3]$ and $[Cr(CO)_5]$ have similar bimolecular rate constants for the reaction with CO.[21-23]

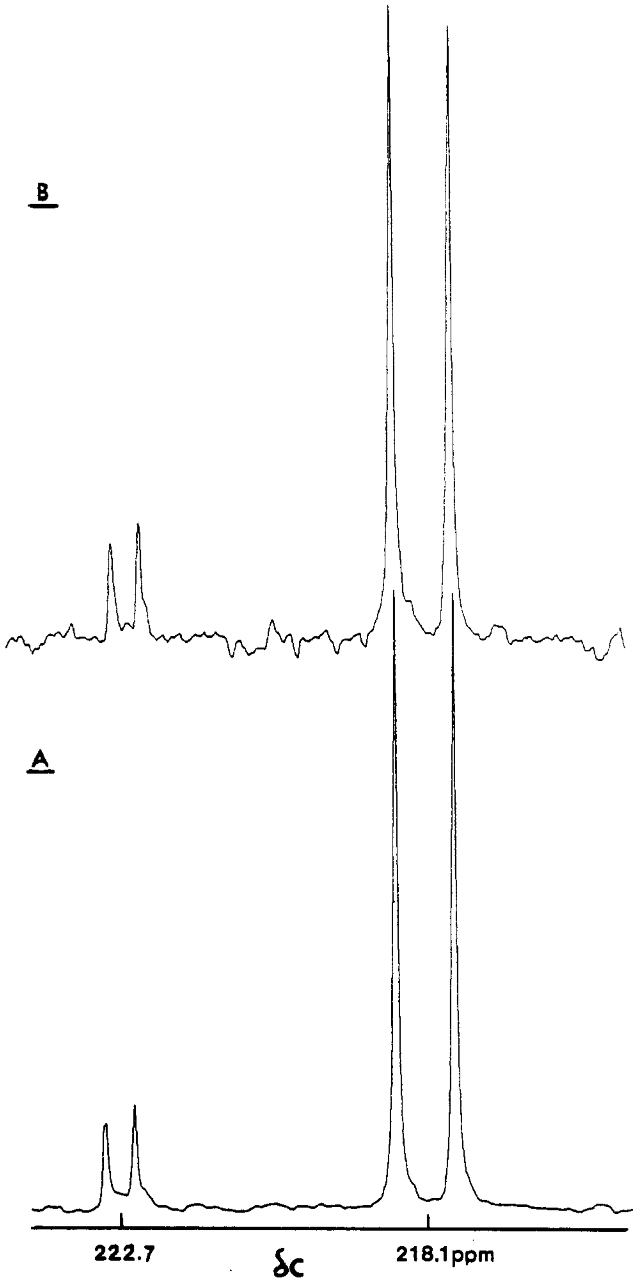


Figure 3. ^{13}C NMR spectra in carbonyl region of $Cr(CO)_5PPh_3$ in toluene-d_8: A, 23 °C, $\delta(C_{\text{trans}})$ 222.7 (J_{P-C} = 6.8 Hz) and $\delta(C_{\text{cis}})$ 218.1 (J_{P-C} = 13.2 Hz); B, 80 °C, $\delta(C_{\text{trans}})$ 222.5 (J_{P-C} = 6.4 Hz) and $\delta(C_{\text{cis}})$ 218.1 (J_{P-C} = 13.2 Hz).

Presumably, the pathway for this nondissociative, intramolecular rearrangement process in d^6 octahedral complexes proceeds through either a trigonal-prismatic[24-29] or bicapped-tetrahedron[30] intermediate or transition state. The relative energy barrier to intramolecular ligand rearrangement as a function of metal has been found to be Cr < W < Mo.[11] Although this is somewhat unexpected based on steric constraints alone, where a greater ease of flexibility for a trigonal twist would be anticipated for the larger Mo and W species, it is evident that electronic factors are important in these

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(20) Unlike this chromium reaction where ΔH^* and ΔS^* indicate a simple dissociative process as the rate-determining step, in the corresponding molybdenum system[4d] a great deal of ligand rearrangement is suggested in the transition state (large negative ΔS^*). This could imply that there is a motion toward the cis configuration (minimizing mutually trans CO ligands) as the Mo–P bonds lengthen in the transition state prior to PPh_3 dissociation.
(21) $[Cr(CO)_5]$ generated by flash photolysis of $Cr(CO)_6$ has been reported to react with CO in cyclohexane with a bimolecular rate constant of $(3 \pm 1) \times 10^6$ M^{-1} s^{-1}.[18] Since [CO] in cyclohexane is $\sim 1.1 \times 10^{-2}$ M,[22] the inverse lifetime of $[Cr(CO)_5]$ in cyclohexane saturated with CO is expected to be about 3×10^4 s^{-1}.
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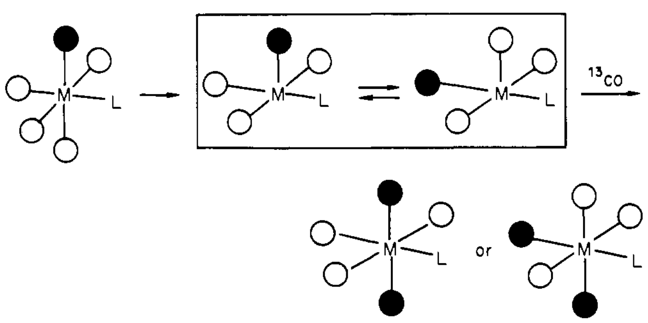
Scheme II



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

$$cis\text{-MO(CO)}_4(\text{PR}_3)_2 \rightleftharpoons trans\text{-Mo(CO)}_4(\text{PR}_3)_2 \qquad (6)$$
$$\text{PR}_3 = \text{PEt}_3 \text{ or P-}n\text{-Bu}_3$$

occurs wth $\Delta H^* = 24.5$ kcal mol^{-1}.[31] On the other hand, CO stereomobility in the $Mo(CO)_5PR_3$ derivatives is apparently a more energetic process than ligand dissociation where $E_a >$ 30 kcal mol^{-1}.[32]

Thus far in our investigations of ligand stereomobility in $M(CO)_5L$ derivatives by nondissociatve routes we have observed this occurrence in chromium and tungsten complexes containing a number of phosphorus donor ligands, including those where L = PPh_3, PPh_2Me, and $P(OMe)_3$. Although activation parameters have not as yet been determined for these rearrangements, it is apparent that ΔH^* is less than that corresponding to ligand dissociation (i.e., <32 kcal mol^{-1}) and greater than 16 kcal mol^{-1}. This latter lower limit is suggested by the lack of line broadening in the ^{13}C NMR of the carbonyl resonances in the high-temperature spectra of these derivatives.[33] More definitive assessments of activation parameters for ligand scrambling in $M(CO)_5PR_3$ species (M = Cr or 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.[34]

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Registry No. *trans*-$Cr(CO)_4(PPh_3)_2$, 38800-75-8; *cis*-$Cr(CO)_4$-(^{13}CO)PPh_3, 81316-24-7; $[Et_4N][CO)_4(PPh_3)Cl]$, 64654-62-2; CO, 630-08-0.

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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 arylsulfonyl halides by noble-metal complexes[1] include the attachment of the arylsulfonyl 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.[2] 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.[2a,b] Desulfonylation of *trans*-$[PtL_2(RSO_2)Cl]$ (where L is PPh_3[3] or PMe_2Ph[4] 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.[2] However, $[Pt(PEt_3)_2Cl(p\text{-tol-}SO_2)]$ cannot be desulfonylated.[4] We have also observed that thermal desulfonylation is not facile for (alkylsulfinato)platinum(II) complexes. The difficulty of extrusion of SO_2 from transition-metal sulfinates has been attributed at least in part to the strength of the metal–sulfur bond.[2b] Since silver ion abstraction of chloride from the acyl complexes $[Pt(PPh_3)_2(RCO)Cl]$ promotes facile alkyl and aryl migration from CO to Pt,[5] it was of interest to determine if similar chloride abstraction from sulfinato complexes $[Pt(PPh_3)_2(RSO_2)Cl]$ would lead to alkyl- and arylplatinum complexes.

Experimental Section

Alkyl- and arylsulfonyl chlorides were distilled or sublimed before use. Benzene was distilled from P_2O_5 and stored over molecular sieves. $Pt(PPh_3)_4$ and $[Pt(PPh_3)_2C_2H_4]$ were prepared by the usual methods.[6,7] 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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