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Chemistry of Metal Hydrides. 25. Reactions of *trans*-$[PtH_2(P\text{-}c\text{-}Hx_3)_2]$ with Carbon Monoxide and Other π Acids

Gordon K. Anderson, Howard C. Clark,* and Julian A. Davies

Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry, University of Guelph, Guelph, Ontario N1G 2W1 Canada

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The complex *trans*-$[PtH_2(P\text{-}c\text{-}Hx_3)_2]$ reacts with carbon monoxide at low temperature to yield $[Pt(CO)_2(P\text{-}c\text{-}Hx_3)_2]$, the reductive elimination of H_2 being reversible at 298 K. The platinum(0) complex undergoes trimerization on warming to ambient temperature to give $[Pt_3(CO)_3(P\text{-}c\text{-}Hx_3)_3]$; it gives $[Pt(CO)_2(P\text{-}c\text{-}Hx_3)(P\text{-}n\text{-}Bu_3)]$ when treated with P-*n*-Bu_3 and reacts with iodine to produce *trans*-$[PtI_2(P\text{-}c\text{-}Hx_3)_2]$. No reaction of *trans*-$[PtH_2(P\text{-}c\text{-}Hx_3)_2]$ with ethylene occurs, but with C_2F_4 insertion into one of the Pt–H bonds takes place. With tetracyanoethylene a 1:1 adduct is formed at 213 K which, on warming to ambient temperature, loses HCN to give *trans*-$[PtH\{C(CN){=}C(CN)_2\}(P\text{-}c\text{-}Hx_3)_2]$.

Introduction

In many homogeneous catalytic systems, one of the key steps is believed to be the insertion of unsaturated, organic molecules into metal–hydrogen bonds.[1] Within this context, reactions of hydridoplatinum(II) complexes, *trans*-$[PtHX(PR_3)_2]$, with olefins[2–5] and acetylenes[6–8] have been extensively studied. Four-coordinate cationic complexes, formed by anion displacement, and/or five-coordinate intermediates have been proposed[3] during the insertion of olefins into the platinum–hydrogen bond.

Dihydridoplatinum(II) complexes, stabilized by bulky tertiary phosphines, have recently become available.[9–11] These complexes do not possess a readily displaceable anionic ligand, and the sterically crowded platinum center[12] would not be expected to react via a five-coordinate intermediate, yet we have found that such complexes exhibit a surprisingly high reactivity toward unsaturated, organic molecules.

A preliminary report from this laboratory has shown that *trans*-$[PtH_2(P\text{-}c\text{-}Hx_3)_2]$ (c-Hx = cyclohexyl) reacts with activated acetylenes to give the corresponding hydrido(alkenyl)platinum(II) complexes,[11] and the involvement of free radical intermediates has been found.[13] The reactions with carbon dioxide[14] and carbon disulfide[15] have also been described. We here report the reactions of *trans*-$[PtH_2(P\text{-}c\text{-}Hx_3)_2]$ with carbon monoxide (for a preliminary report see ref 16) and a number of olefins, which lead to a diverse range of products.

Results and Discussion

It was previously noted[16] that when a benzene solution of *trans*-$[PtH_2(P\text{-}c\text{-}Hx_3)_2]$ was treated with carbon monoxide at ambient temperature, it became red, and the isolated product was tentatively assigned as the trimeric complex $[Pt_3(CO)_3(P\text{-}c\text{-}Hx_3)_3]$. No attempt was made at that stage, however, to determine the mechanism by which $[Pt_3(CO)_3(P\text{-}c\text{-}Hx_3)_3]$ was produced. The structures of the complexes $[Pt_3(CO)_3(P\text{-}c\text{-}Hx_3)_3]$[17] and $[Pt_3(CO)_3(P\text{-}c\text{-}Hx_3)_4]$[18] had previously been determined.

When carbon monoxide was passed through a toluene solution of *trans*-$[PtH_2(P\text{-}c\text{-}Hx_3)_2]$ at 213 K no color change was evident, but the $^{31}P\{^1H\}$ NMR spectrum at this temperature indicated that quantitative formation of a new species ($\delta(P)$ 20.2 ($^1J(Pt\text{–}P)$ = 3123 Hz) had occurred. After a similar solution of *trans*-$[PtH_2(P\text{-}c\text{-}Hx_3)_2]$ was stirred under 1 atm of carbon-13 monoxide at 233 K, the $^{13}C\{^1H\}$ NMR spectrum exhibited a triplet resonance at $\delta(C)$ 185.0 ($^2J(P\text{–}C)$ = 12 Hz) with ^{195}Pt satellites ($^1J(Pt\text{–}C)$ = 1809 Hz), indicating the presence of only one CO environment. Such a chemical shift is more reminiscent of a terminal carbonyl attached to platinum[19] than of a metal–formyl group,[20] which might have been formed by insertion of CO into a Pt–H bond, and the multiplicity is due to coupling to two equivalent phosphorus nuclei. The $^{31}P\{^1H\}$ NMR spectrum of such a solution also contained triplet resonances, indicating the presence of two equivalent carbonyl groups. Thus, the new species is formulated as the platinum(0) complex $[Pt(CO)_2(P\text{-}c\text{-}Hx_3)_2]$.

This formulation is consistent with the observation that when a toluene-d_8 solution of *trans*-$[PtH_2(P\text{-}c\text{-}Hx_3)_2]$ was treated with carbon monoxide at 213 K, the ^1H NMR spectrum indicated that complete reaction had taken place, as evidenced by the disappearance of the hydride resonance at $\delta(H)$ −3.35. The lack of any new resonances

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suggests that reductive elimination of dihydrogen occurs on treatment of the complex with carbon monoxide. While CO insertion into metal–carbon bonds is well documented,[21] the insertion of CO into a metal–hydrogen bond to yield a metal–formyl complex[22] in this case is obviously a less favored process.

When the passage of carbon monoxide was continued at ambient temperature, the solution rapidly became red. From such a solution were obtained orange-red crystals of the trimeric complex $[Pt_3(CO)_3(P\text{-}c\text{-}Hx_3)_3]$, which was identified by its characteristic $^{31}P\{^1H\}$ NMR spectrum (δ(P) 71.0 (^1J(Pt–P) = 4409 Hz, ^2J(Pt–P) = 409 Hz, ^1J(P–P) = 55 Hz, ^1J(Pt–Pt) = 1633 Hz)).[23] If $[Pt(CO)_2(P\text{-}c\text{-}Hx_3)_2]$ was prepared at 213 K and free CO was removed from the system by purging with a stream of nitrogen before warming to ambient temperature, however, the solution only slowly became red and, after it was left standing for 24 h, the $^{31}P\{^1H\}$ NMR spectrum showed that $[Pt(CO)_2(P\text{-}c\text{-}Hx_3)_2]$ was still the major phosphorus-containing species in solution. A broad resonance at δ(P) 19.8 was previously observed for such a solution, but this was not recognized as an intermediate in the reaction sequence and was erroneously attributed to a rapid equilibrium between the species $[Pt_3(CO)_3(P\text{-}c\text{-}Hx_3)_3]$ and $[Pt_3(CO)_3(P\text{-}c\text{-}Hx_3)_4]$.[16]

The reductive elimination of H_2 from *trans*-$[PtH_2(P\text{-}c\text{-}Hx_3)_2]$ was found to be irreversible at low temperature, but when hydrogen gas was passed through a solution of $[Pt(CO)_2(P\text{-}c\text{-}Hx_3)_2]$ for 5 min at 213 K (to remove free CO and hence reduce the rate of trimerization), followed by 30 min at ambient temperature, regeneration of the dihydridoplatinum(II) complex occurred. No resonances due to organic species were detected in the ^1H NMR spectrum of such a solution, demonstrating that the elimination of carbon monoxide occurs without its reduction. Reductive elimination of H_2 from transition-metal complexes by displacement with carbon monoxide has also been shown to be reversible in certain other cases.[24]

In the absence of a nucleophile such as carbon monoxide, the reductive elimination of H_2 is extremely slow. Indeed, when a solution of *trans*-$[PtH_2(P\text{-}c\text{-}Hx_3)_2]$ was heated to 423 K in vacuo, the reaction was incomplete after 4 days, the new species formed being identified by its $^{31}P\{^1P\}$ NMR spectrum as $[Pt(P\text{-}c\text{-}Hx_3)_2]$ (δ(P) 61.1 (^1J(Pt–P) = 4180 Hz)). It is not surprising that such vigorous conditions should be necessary to promote this reaction, because *trans*-$[PtH_2(P\text{-}c\text{-}Hx_3)_2]$ may be prepared by oxidative addition of H_2 to the bis(phosphine)platinum(0) complex at ambient temperature.[9,10] The previously proposed mechanism for the carbonylation of *trans*-$[PtH_2(P\text{-}c\text{-}Hx_3)_2]$, namely, initial reduction to give $[Pt(P\text{-}c\text{-}Hx_3)_2]$ followed by reaction with CO to yield $[Pt_3(CO)_3(P\text{-}c\text{-}Hx_3)_3]$ and free tricyclohexylphosphine,[16] is clearly inconsistent with these observations, nucleophilic attack of carbon monoxide on the dihydridoplatinum(II) complex being the initial step. When a *trans*-$[PtH_2(P\text{-}c\text{-}Hx_3)_2]$ solution was heated in the presence of oxygen the bis(phosphine)platinum(0) complex was readily oxidized to give $[PtO_2(P\text{-}c\text{-}Hx_3)_2]$ (δ(P) 25.0 (^1J(Pt–P) = 3940 Hz)).

When a toluene solution of $[Pt(CO)_2(P\text{-}c\text{-}Hx_3)_2]$ at 213 K was treated with 1 molar equiv of tri-*n*-butylphosphine, the mixed phosphine complex $[Pt(CO)_2(P\text{-}c\text{-}Hx_3)(P\text{-}n\text{-}Bu_3)]$ (δ(P-c-Hx_3) 24.2 (^1J(Pt–P) = 3064 Hz), δ(P-*n*-Bu_3) −24.4 (^1J(Pt–P) = 3230 Hz, ^2J(P–P) = 15 Hz)) was produced, along with free tricyclohexylphosphine (δ(P) 7.0). With a second molar equivalent an equilibrium was set up, involving the mixed phosphine complex and $[Pt(CO)_2(P\text{-}n\text{-}Bu_3)_2]$ (δ(P)-19.3 (^1J(Pt–P) = 3191 Hz). The displacement of tertiary phosphine is unusual, since addition of a nucleophile to complexes of the type $[Pt(CO)_2(PR_3)_2]$ normally results in loss of carbon monoxide.[25] The preferential displacement of P-c-Hx_3 in this case is likely to be due to the relief of steric crowding afforded in the platinum(0) complex, and this might also be an important factor in the ready formation of $[Pt_3(CO)_3(P\text{-}c\text{-}Hx_3)_3]$, where dissociation of P-c-Hx_3 may be promoted thermally by warming a $[Pt(CO)_2(P\text{-}c\text{-}Hx_3)_2]$ solution to ambient temperature.

Similar treatment of $[Pt(CO)_2(P\text{-}c\text{-}Hx_3)_2]$ with other nucleophiles, including *tert*-butyl isocyanide, pyridine, and dimethyl sulfide, did not result in such clean reactions. With each of these ligands no reaction took place at 213 K, while at ambient temperature displacement of both tertiary phosphine ligands occurred, accompanied by extensive decomposition, giving no phosphorus-containing platinum species.

When excess iodine was introduced to a toluene solution of $[Pt(^{13}CO)_2(P\text{-}c\text{-}Hx_3)_2]$ at 213 K the $^{31}P\{^1H\}$ NMR spectrum, after 2 h at this temperature, indicated that complete reaction of the zerovalent platinum complex had occurred. Almost total conversion to *trans*-$[PtI_2(P\text{-}c\text{-}Hx_3)_2]$ (δ(P) 9.3 (^1J(Pt–P) = 2253 Hz)) was evident, while a trace of *cis*-$[PtI_2(^{13}CO)(P\text{-}c\text{-}Hx_3)]$ (δ(P) 33.6 (^1J(Pt–P) = 2788 Hz, ^2J(P–C) = 5 Hz)) was also observed. It was previously found that $[Pt_3(CO)_3(P\text{-}c\text{-}Hx_3)_3]$ underwent reaction with iodine to yield *cis*-$[PtI_2(CO)(P\text{-}c\text{-}Hx_3)]$,[16] so it may be that the latter species formed in this case was obtained by reaction of a trace of the trimeric complex present in the solution.

It is perhaps surprising that displacement of P-c-Hx_3 from $[Pt(CO)_2(P\text{-}c\text{-}Hx_3)_2]$ occurs on addition of P-*n*-Bu_3 at 213 K, while the reaction with iodine causes displacement of carbon monoxide. It has been suggested (vide supra) that loss of P-c-Hx_3, rather than CO, to give $[Pt(CO)_2(P\text{-}c\text{-}Hx_3)(P\text{-}n\text{-}Bu_3)]$ occurs because it involves a reduction in steric crowding in the platinum(0) product. While four-coordinate platinum(0) complexes adopt a geometry approaching tetrahedral, their divalent counterparts are square planar and, by forming a complex of trans configuration, may be less sterically hindered. However, on purely steric grounds, the complex *trans*-$[PtI_2(P\text{-}c\text{-}Hx_3)_2]$, which contains the bulkiest of halides, would be expected to be relatively crowded and so *cis*-$[PtI_2(CO)(P\text{-}c\text{-}Hx_3)]$ may possibly be the preferred steric product. Electronically, however, the two strong σ-donor phosphine ligands may roughly balance the electronegative halides in the *trans*-$[PtI_2(P\text{-}c\text{-}Hx_3)_2]$ complex, whereas in *cis*-$[PtI_2(CO)(P\text{-}c\text{-}Hx_3)]$, the π-acid carbonyl ligand would result in a electron-poor metal center. Thus for the former complex, where the bulky tricyclohexylphosphine ligands make an angle of about 180° at platinum,[26] the course of the reaction is determined by the steric requirements of the products and also the valence of the metal center (i.e., electronically). The reactions of $[Pt(CO)_2(P\text{-}c\text{-}Hx_3)_2]$ are summarized in Scheme I .

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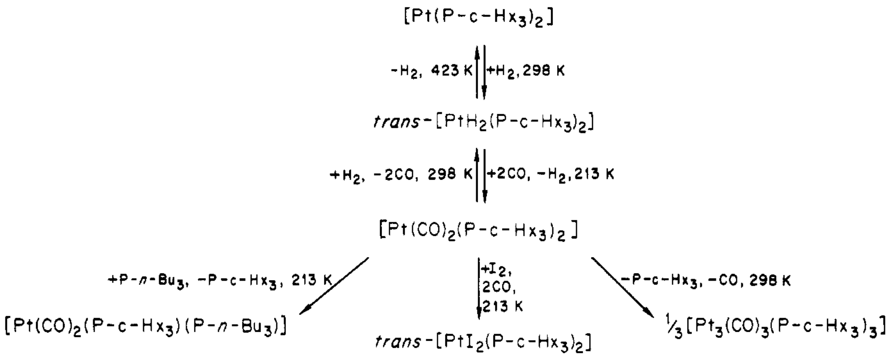
Scheme I



It has previously been observed that *trans*-[PtH_2(P-c-$Hx_3)_2$] reacts with substituted acetylenes, only if they contain electron-withdrawing substituents.[11,13] A similar situation has been found to prevail for the analogous reactions with olefinic compounds.

When ethylene was passed through a toluene solution of *trans*-[PtH_2(P-c-$Hx_3)_2$] at ambient temperature for 1 h, the $^{31}P\{^1H\}$ NMR spectrum indicated that no reaction had taken place. With tetrafluoroethylene, however, a slow reaction took place, which was complete after passing the gas through a solution of *trans*-[PtH_2(P-c-$Hx_3)_2$] at ambient temperature for 3 h or after stirring under 1 atm of C_2F_4 for 2 days. The complex isolated from this reaction was *trans*-[PtH(CF_2CF_2H)(P-c-$Hx_3)_2$], formed by insertion of the olefin into one of the platinum–hydrogen bonds. Its $^{31}P\{^1H\}$ NMR spectrum consisted of a triplet resonance (^3H(P–F) = 15 Hz), due to coupling to the two α-fluorine nuclei, with ^{195}Pt satellites, while the ^{1}H NMR spectrum exhibited a hydride resonance at δ(H) −9.95, which was a complex multiplet due to coupling to two phosphorus and two fluorine nuclei. The low ^1J(Pt–H) value of 520 Hz is consistent with the hydride being trans to an alkyl moiety. The analytical data (see Experimental Section) also support this formulation.

These observations are similar to those for the reactions of the dihydridoplatinum(II) complex with acetylenes, where no interaction with the unsubstituted compound was found. Also, both hexafluorobut-2-yne and tetrafluoroethylene insert into only one of the P–H bonds.

A reaction of *trans*-[PtH_2(P-c-$Hx_3)_2$] with tetracyanoethylene was found to occur even at 213 K. When 1 molar equiv of the olefin was added to a toluene solution of *trans*-[PtH_2(P-c-$Hx_3)_2$] at this temperature, a pale green solution resulted. The $^{31}P\{^1H\}$ NMR spectrum of this solution indicated quantitative formation of a new species (δ(P) 34.5 (^1J(Pt–P) = 2695 Hz)), which underwent further reaction on warming to ambient temperature. The second stage of the reaction was promoted by heating to 348 K for 1 h and the final product was isolated and identified as *trans*-[PtH{C(CN)═C(CN)$_2$}(P-c-$Hx_3)_2$]. Its infrared spectrum exhibited a band at 1595 cm^{-1}, indicative of the alkenyl moiety, and bands at 2192, 2168, and 2144 cm^{-1}, due to ν(Pt—H) and ν(C≡N). The ^{1}H NMR spectrum contained a triplet resonance at δ(H) −8.41 (^2J(P–H) = 14 Hz) with ^{195}Pt satellites (^1J(Pt–H) = 777 Hz), and the relatively low value of ^1J(Pt–H) is consistent with the hydride lying trans to a ligand of high trans influence such as an alkenyl group. The formulation of the final product as *trans*-[PtH{C(CN)═C(CN)$_2$}(P-c-$Hx_3)_2$] is also supported by analytical data (see Experimental Section).

The nature of the intermediate species was investigated by ^{1}H NMR spectroscopy. When a toluene-d_8 solution of *trans*-[PtH_2(P-c-$Hx_3)_2$] was treated with tetracyanoethylene at 213 K, a new hydride resonance was observed at δ(H) −18.06, with a one-bond coupling to platinum-195 of 1146 Hz. This relatively high value of ^1J(Pt–H) is unlikely to be due to a hydride lying trans to an alkyl group, formed by insertion of $C_2(CN)_4$ into a platinum–hydrogen bond, and is more consistent with a 1:1 adduct, [PtH_2(P-c-$Hx_3)_2$ {(NC)$_2$C═C(CN)$_2$}].

In support of this formulation, similar adducts of the type [PtHX($PR_3)_2${(NC)$_2$C═C(CN)$_2$}] (R = Et or Ph; X = Cl, Br, or CN) have been proposed[27] as intermediates in the reaction of *trans*-[PtHX($PR_3)_2$] with tetracyanoethylene. Indeed, one such adduct has been isolated (R = Et; X = CN).[27]

Despite the sterically crowded nature of the metal center in *trans*-[PtH_2(P-c-$Hx_3)_2$],[12] adduct formation is clearly possible in certain, favorable circumstances. In the present case, the planar tetracyanoethylene molecule[28] may approach the platinum center perpendicular to the PtP_2 axis, thus minimizing interactions with the bulky cyclohexyl groups. This is in agreement with the general observation that the olefinic moiety in platinum(II) olefin complexes lies perpendicular to the square plane containing the metal center.[29]

It is interesting that reductive elimination of HX from [PtHX($PR_3)_2${(NC)$_2$C═C(CN)$_2$}] took place[27] to yield the platinum(0) complex, [Pt($PR_3)_2${(NC)$_2$C═C(CN)$_2$}]. Here it is found that [PtH_2(P-c-$Hx_3)_2${(NC)$_2$C═C(CN)$_2$}] reacts thermally by elimination of HCN to give an alkenylplatinum(II) complex. Similar chemistry has been observed for an iridium(III) species.[30]

These results show that *trans*-[PtH_2(P-c-$Hx_3)_2$] may undergo reductive elimination of H_2, insertion of an unsaturated molecule into a Pt–H bond or adduct formation, followed by elimination of HCN, the course of the reaction being determined by the nature of the added ligand. These, and subsequent reactions of [Pt(CO)$_2$(P-c-$Hx_3)_2$], demonstrate the high degree steric control involved in the reactions of platinum complexes containing tricyclohexylphosphine.[31]

Experimental Section

The ^{1}H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded at 60.0, 15.1, and 24.3 MHz, respectively, on a Brüker WP-60 spectrometer operating in the Fourier transform mode. ^{1}H and ^{13}C chemical shifts are relative to Me_4Si (internal) and ^{31}P chemical shifts are relative to H_3PO_4 (external), more positive values representing deshielding. Infrared spectra were measured for Nujol mulls between CsI plates, using a Perkin Elmer 180

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spectrophotometer. Elemental analyses were performed by Guelph Chemical Laboratories Ltd.

Carbon-13 labeled carbon monoxide (90% enriched) was obtained from Prochem, tetrafluoroethylene was supplied by PCR Research Chemicals Inc., and tetracyanoethylene was obtained from Aldrich.

The complex *trans*-[PtH$_2$(P-c-Hx$_3$)$_2$] was prepared by treating *trans*-[PtHCl(P-c-Hx$_3$)$_2$] with NaBH$_4$ in ethanol.[32]

Reaction of *trans*-[PtH$_2$(Pt-c-Hx$_3$)$_2$] with Carbon Monoxide. *trans*-[PtH$_2$(P-c-Hx$_3$)$_2$] was dissolved in toluene and the solution was cooled to 213 K. Carbon monoxide was passed through the solution for 1 h (or, where ^{13}CO was used, the solution was stirred under 1 atm of the gas for 3 h), resulting in quantitative conversion to the complex [Pt(CO)$_2$(P-c-Hx$_3$)$_2$] (δ(P) 20.2 (^1J(Pt–P) = 3123 Hz); δ(C) 185.0 (^1J(Pt–C) = 1809 Hz, ^2J(P–C) 12 Hz)). When excess CO was removed by purging the solution with nitrogen, the major species present after standing for 24 h at ambient temperature was still [Pt(CO)$_2$(P-c-Hx$_3$)$_2$], but when the solution was allowed to warm in the presence of free CO, it rapidly became red and its ^{31}P{^{1}H} NMR spectrum indicated the presence of free P-c-Hx$_3$ (δ(P) 7.0) and [Pt$_3$(CO)$_3$(P-c-Hx$_3$)$_3$] (δ(P) 71.0 (^1J(Pt–P) = 4409 Hz, ^2J(Pt–P) = 409 Hz, ^3J(P–P) = 55 Hz, ^1J(Pt–Pt) = 1633 Hz)), when the spectrum was recorded at 213 K.

Thermal Decomposition of *trans*-[PtH$_2$(P-c-Hx$_3$)$_2$]. A toluene-d_8 solution of *trans*-[PtH$_2$(P-c-Hx$_3$)$_2$] was sealed in a NMR tube under vacuum and heated to 423 K. After 4 days the signal at δ(H) −3.35 in the ^{1}H NMR spectrum had diminished in intensity, and after 11 days it had disappeared completely. In the ^{31}P{^{1}H} NMR spectrum the resonance due to *trans*-[PtH$_2$(P-c-Hx$_3$)$_2$] was replaced by one associated with [Pt(P-c-Hx$_3$)$_2$] (δ(P) 61.1 (^1J(Pt–P) = 4180 Hz)). When the solution was heated in air, the complex [PtO$_2$(P-c-Hx$_3$)$_2$] (δ(P) 25.0 (^1J(Pt–P) = 3940 Hz)) was produced.

Reaction of [Pt(CO)$_2$(P-c-Hx$_3$)$_2$] with Tri-*n*-butylphosphine. To a solution of [Pt(CO)$_2$(P-c-Hx$_3$)$_2$], prepared by treatment of *trans*-[PtH$_2$(P-c-Hx$_3$)$_2$] with carbon monoxide in toluene at 213 K, was added 1 mol equiv of P-*n*-Bu$_3$. The ^{31}P{^{1}H} NMR spectrum at 213 K indicated the formation of [Pt(CO)$_2$(P-c-Hx$_3$)(P-*n*-Bu$_3$)] (δ(P-c-Hx$_3$) 24.2 (^1J(Pt–P) = 3064 Hz); δ(P-*n*-Bu$_3$) −24.4 (^1J(Pt–P) = 3230 Hz, ^2J(P–P) = 15 Hz)) and free P-c-Hx$_3$ (δ(P) 7.0). Addition of further P-*n*-Bu$_3$ resulted in some formation of [Pt(CO)$_2$(P-*n*-Bu$_3$)$_2$] (δ(P) −19.3 (^1J(Pt–P) = 3191 Hz)).

Similar treatment of [Pt(CO)$_2$(P-c-Hx$_3$)$_2$] with CN-*t*-Bu (1 mol equiv), Me$_2$S, or pyridine (excess) caused no reaction at 213 K, while displacement of P-c-Hx$_3$ (δ(P) 7.0) occurred at ambient temperature, accompanied by extensive decomposition.

Reaction of [Pt(CO)$_2$(P-c-Hx$_3$)$_2$] with Iodine. Excess iodine was added to a toluene solution of [Pt(^{13}CO)$_2$(P-c-Hx$_3$)$_2$] at 213 K and, after the solution was left standing at this temperature for 2 h, the ^{31}P{^{1}H} NMR spectrum contained resonances due to *trans*-[PtI$_2$(P-c-Hx$_3$)$_2$] (δ(P) 9.3 (^1J(Pt–P) = 2253 Hz)) and a very minor amount of *cis*-[PtI$_2$(^{13}CO)(P-c-Hx$_3$)] (δ(P) 33.6 (^1J(Pt–P) = 2788 Hz, ^2J(P–C) 5 Hz)).

Reaction of *trans*-[PtH$_2$(P-c-Hx$_3$)$_2$] with Tetrafluoroethylene. A benzene solution of *trans*-[PtH$_2$(P-c-Hx$_3$)$_2$] was stirred under 1 atm of C$_2$F$_4$ for 2 days, which resulted in complete reaction to give *trans*-[PtH(CF$_2$CF$_2$H)(P-c-Hx$_3$)$_2$] (δ(P) 36.9 (^1J(Pt–P) = 2905 Hz, ^3J(P–F) 15 Hz); δ(H) −9.95 (^1J(Pt–H) = 520 Hz, ^2J(P–H) = 16 Hz, ^3J(F–H) = 3 Hz)). Slow evaporation of the solvent allowed isolation of colorless crystals. (Anal. Calcd for $C_{38}H_{68}F_4P_2Pt$: C, 53.21; H, 8.00; F, 8.87. Found: C, 53.11; H, 8.13; F, 8.96.)

Reaction of *trans*-(PtH$_2$(P-c-Hx$_3$)$_2$] with Tetracyanoethylene. Tetracyanoethylene (1 mol equiv) was added to a toluene solution of *trans*-[PtH$_2$(P-c-Hx$_3$)$_2$] at 213 K, giving a pale green solution, and quantitative formation of a new species (δ(P) 34.5 (^1J(Pt–P) = 2695 Hz); δ(H) −18.06 (^1J(Pt–H) = 1146 Hz, ^2J(P–H) 12 Hz)) resulted. Heating to 348 K for 1 h caused complete conversion to *trans*-[PtH{C(CN)=C(CN)$_2$}(P-c-Hx$_3$)$_2$] (δ(P) 37.5 (^1J(Pt–P) = 2603 Hz); δ(H) −8.41 (^1J(Pt–H) = 777 Hz, ^2J(P–H) = 14 Hz)) and, after treatment with charcoal and filtration, slow evaporation of the solvent produced yellow crystals. (Anal. Calcd for $C_{41}H_{67}N_3P_2Pt$: C, 57.34; H, 7.87; N, 4.90. Found: C, 56.64; H, 8.08; N, 4.68. IR data: ν(C=C) 1595 cm^{-1}, ν(Pt—dH) and ν(C≡N) 2192, 2168, and 2144 cm^{-1}.)

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Registry No. *trans*-[PtH$_2$(P-c-Hx$_3$)$_2$], 42764-83-0; Pt(CO)$_2$(P-c-Hx$_3$)$_2$, 79769-84-9; Pt$_3$(CO)$_3$(P-c-Hx$_3$)$_3$, 62987-80-8; Pt(CO)$_2$(P-c-Hx$_3$)(P-*n*-Bu$_3$), 79769-85-0; Pt(CO)$_2$(P-*n*-Bu$_3$)$_2$, 79769-86-1; *trans*-[PtI$_2$(P-c-Hx$_3$)$_2$, 53856-43-2; *cis*-[PtI$_2$(Co)(P-c-Hx$_3$), 79813-73-3; *trans*-[PtH(CF$_2$CF$_2$H)(P-c-Hx$_3$)$_2$, 79769-87-2; *trans*-[PtH{C(CN)=C(CN)$_2$}(P-c-Hx$_3$)$_2$, 79769-88-3; C$_2$F$_4$, 116-14-3; (NC)$_2$C=C(CN)$_2$, 670-54-2; PtH$_2$(P-c-Hx$_3$)$_2${(NC)$_2$C=C(CN)$_2$}, 79769-89-4.

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Silicon in Synthesis. 14. (Methoxy(trimethylsilyl)methyl)lithium. A New Reagent for Carbonyl Homologation

Philip Magnus*[1] and Glenn Roy

Evans Chemistry Laboratory, The Ohio State University, Columbus, Ohio 43210

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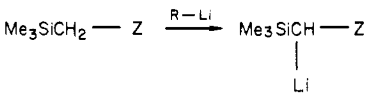
(Methoxy(trimethylsilyl)methyl)lithium (8) is generated by treatment of (methoxymethyl)trimethylsilane with *sec*-butyllithium. The reagent 8 reacts with aldehydes and ketones to give 1:1 adducts that are readily transformed into enol ethers, aldehydes, methoxymethyl alcohols, and methoxymethyl ketones.

Introduction

During the past decade or so a wide range of organosilicon reagents has been developed for use in organic synthesis.[2] Many of these reagents utilize the ability of the trimethylsilyl group to stabilize an adjacent carbon–metal bond. In general, for convenience, the choice of the

Scheme I



$$\mathrm{Me_3SiCH_2}-\mathrm{Z} \xrightarrow{\mathrm{R-Li}} \mathrm{Me_3Si}\underset{\substack{|\\ \mathrm{Li}}}{\mathrm{CH}}-\mathrm{Z}$$

1

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[1] To whom correspondence should be addressed at Indiana University, Department of Chemistry, Bloomington, IN 47405.

[2] For recent reviews see: Fleming, I. In "Comprehensive Organic Chemistry"; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon Press: Oxford, 1979; p 761. Magnus, P. *Aldrichimica Acta* **1980**, *13*, 43.