ORGANOMETALLICS

Intermolecular Methyl Group Exchange and Reversible P–Me Bond Cleavage at Cobalt(III) Dimethyl Halide Species

Hongwei Xu, Paul G. Williard, and Wesley H. Bernskoetter*

Department of Chemistry, Brown University, Providence, Rhode Island 02912, United States

Supporting Information

ABSTRACT: The cobalt(III) dimethyl halide complexes $cis,mer-(PMe_3)_3Co(CH_3)_2X$ (X = Cl, I) were found to undergo a degenerate cobalt-to-cobalt transfer of the methyl ligands during isotopic labeling experiments. Extensive mechanistic studies exclude radical, methyl iodide elimination, and disproportionation/comproportionation pathways for exchange of the methyl groups between metals. A related



cobalt(III) dimethyl complex supported by the tridentate phosphine ligand MeP(CH₂CH₂PMe₂)₂ showed dramatically slower methyl ligand transfer, indicative of a mechanism for intermetallic exchange with a requisite phosphine dissociation. Crossover experiments between cobalt(III) dimethyl halide complexes supported by PMe₃ and MeP(CH₂CH₂PMe₂)₂ are consistent with a dicobalt transition structure in which only one cobalt center requires phosphine dissociation prior to methyl transfer. An additional methyl group scrambling process between $cis,mer-(PMe_3)_3Co(CH_3)_2I$ and free PMe₃ was also identified during the investigation and originates from reversible P-CH₃ bond cleavage.

INTRODUCTION

The transfer of alkyl ligands between metal centers has been observed in a variety of transition metal complexes and may occur via a wide range of potential pathways depending on the coordination, steric, and electronic characteristics of a particular species.¹ The intermolecular exchange of alkyl groups from one metal to another has drawn interest for its relationship to synthetic techniques using main group alkylating agents, the biosynthesis of acetyl coenzyme A, alkyl/aryl scrambling during palladium-catalyzed cross-coupling, and more recently as a proposed intermediate step for oxidative methane oligomerization methods.^{1,2} Metal-to-metal transfer of methyl groups recently garnered the attention of our laboratory over the course of investigations into the mechanism for C-C bond formation at strong field cobalt centers.³ During these studies the cobalt(III) complex $cis_{1}mer-(PMe_{3})_{3}Co(CH_{3})_{2}I$ (1-Me₂) was found to scramble isotopicially labeled methyl ligands between cobalt centers prior to selective reductive carboncarbon bond elimination (Figure 1). Similar intermolecular methyl ligand exchange processes have also been reported for several other late transition metal organometallic species.^{1,2} Preliminary experiments with 1-Me₂ suggested that methyl group exchange persisted even under conditions where C-C reductive elimination was extremely slow, leading to a hypothesis that the two processes may not be intimately linked in mechanism.³ Herein we report the results of a more complete experimental examination of the mechanism for cobalt-to-cobalt methyl group transfer at 1-Me₂, the observation of an unusual phosphorus-methyl bond scission reaction at cobalt, and the synthesis and characterization of a closely related cobalt(III) species, cis,mer-(PMe₃)₃Co(CH₃)₂(SO₃CF₃) $(2-Me_2).$

RESULTS AND DISCUSSION

A diverse range of potential pathways for the intermolecular methyl group exchange observed at 1-Me2 may be proposed on the basis of common transformations for first-row transition metals,⁴ related exchanges with heavier transition metal species, 1c-e,2 and previous examinations of methyl ligand transfer at cobalt.^{1a,f} Guided by these studies, a series of general mechanistic routes for cobalt-methyl exchange were considered, including: a radical crossover mechanism (path A), a methyl iodide elimination route (path B), a cobalt(I)catalyzed disproportionation pathway (path C), a bimetallic exchange derived from iodide loss (path D), and a bimetallic exchange derived from phosphine loss (path E). These mechanisms for cobalt-to-cobalt methyl group transfer in 1-Me₂ were then probed by experimental methods to affirm or discount the probability of each reaction pathway.

Path A: Radical Crossover. The relatively low bond dissociation enthalpy of cobalt-methyl bonds has been demonstrated in multiple studies⁵ and frequently gives rise to the extrusion of methyl radicals.⁶ This feature accounts for much of the reactivity of the cobalamine complex in vitamin B_{12} and could also account for the intermolecular exchange of the methyl ligands in 1-Me₂ (Figure 2; path A).⁷ In fact, it was during isotopic crossover experiments to probe for an outersphere methyl radical mechanism in reductive C-C bond elimination that our laboratory first observed intermolecular methyl transfer in $1-Me_2$.³ Upon heating a mixture of $1-d_3Me_2$ isotopomers to 50 °C (the cobalt methyl ligands undergo rapid intramolecular site exchange at ambient temperature), sub-

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Figure 1. Intermolecular methyl ligand scrambling and ethane reductive elimination from 1-d₃Me₂.



Figure 2. Methyl radical extrusion pathway for methyl group exchange.

stantial quantities of the crossover products, CD_3CD_3 and CH_3CH_3 , were observed (Figure 1). However, the deviation from a statistically expected mixture of isotopologue products (1:2:1 neglecting secondary isotope effects) and their changing ratio over the course of the reaction both hinted that a standard radical or bimetallic elimination pathway was not manifesting in C–C bond formation.³ Careful examination of the crossover experiment at low conversion to ethane revealed intermolecular scrambling of the cobalt—methyl ligands in the reactant prior to elimination, evident from a slight isotopic perturbation of the chemical shifts of the Co–CH₃ signals. In subsequent studies, this intermolecular methyl exchange has also been detected in samples of $1-d_3Me_2$ in benzene- d_6 at ambient temperature over the course of a day (Figure 3; scrambling after 24 h at 23 °C).⁸



Figure 3. Partial ¹H{³¹P} NMR spectrum showing isotopic perturbation of chemical shifts between the Co–CH₃ of 1-Me₂ and 1- d_3 Me₂ at 10 °C in benzene- d_6 .

In order to investigate the intermediacy of methyl radicals in the scrambling of cobalt–alkyl groups in $1-d_3Me_2$, the exchange reaction was monitored in the presence of excess (0.25 M) 1,4cyclohexadiene (CHD). This diene undergoes H atom abstraction by ${}^{\circ}$ CH₃ with a rate constant on the order of 10^{5} M⁻¹ s⁻¹ (27 °C), and thus should make a reasonable probe for the intermediacy of outer-sphere methyl radicals.^{9,10} Significantly, no substantial quantities of methane were detected by NMR spectroscopy during the trapping experiment (<4%) over two days at ambient temperature, and the presence of CHD did not alter the relative half-life of intermolecular methyl exchange compared to parallel control samples without the methyl radical probe. These observations are taken to be inconsistent with an outer-sphere methyl radical crossover pathway (path A).

Path B: Methyl lodide Elimination. The reductive elimination of carbon-halide bonds from transition metals has drawn increasing interest as the microscopic reverse of C-X bond oxidative addition in catalytic cross-coupling reactions as well as for its own utility in catalytic applications.¹¹ Notably, several examples of methyl iodide reductive elimination from heavy metal complexes related to 1-Me₂ have been reported.¹² A process invoking a similar iodomethane elimination from the dimethyl iodide cobalt(III) species could result in intermolecular scrambling of the cobalt-methyl sites (path B; Figure 4). In this case CH₃I eliminated from one metal center would react with the organometallic product of a second methyl iodide elimination to afford the net exchange. Such methyl iodide elimination reactions could presumably occur via either sequential I⁻ loss followed by nucleophilic attack on Co-CH₃ or concerted C-I bond formation.

The reversible methyl iodide elimination pathway was first explored by attempting to observe incorporation of isotopically labeled CD₃I into **1-Me**₂ at ambient temperature over approximately 24 h (conditions where intermolecular methyl group exchange is easily detected by NMR spectroscopy). Unfortunately, addition of 0.5 to 2 equiv of CD₃I to benzene solutions of **1-Me**₂ resulted in degradation of the organometallic species within 30 min, prior to observation of any isotopic exchange.¹³ As a substitute for methyl iodide, a related



Figure 4. Reversible iodomethane elimination pathway for methyl group exchange.

experiment was performed by treating $1-d_6Me_2$ with 1 equiv of methyl trifluoromethanesulfonate (MeOTf) (eq 1). This



reaction resulted in exchange of the iodide and triflate anions, affording *cis,mer*-(PMe₃)₃Co(CD₃)₂OTf ($2-d_6Me_2$) and free iodomethane over one hour. Significantly, no isotopic exchange of the methyl groups was observed in the iodomethane or cobalt product by ¹H or ²H NMR spectroscopy. The cobalt(III) dimethyl triflate complex may alternatively be prepared by addition of MeOTf to (PMe₃)₄CoCH₃ (eq 2), with complete



conversion occurring within two hours. The cobalt dimethyl triflate species was characterized in its perprotio isotopologue (2-Me₂) by variable-temperature NMR spectroscopy, combustion analysis, and single-crystal X-ray diffraction.¹⁴ At ambient temperature the ¹H and ³¹P NMR spectra of 2-Me₂ exhibit broad resonances indicative of a dynamic molecular process close to the time scale of the NMR experiment.¹⁵ Cooling the sample to -40 °C in toluene- d_8 afforded sharp spectral features, including two Co-CH₃ resonances at 0.72 and -1.65 ppm in the ¹H NMR spectrum as well as a doublet and triplet at 9.09 and -5.95 ppm in the ³¹P NMR spectrum. The molecular structure of 2-Me2 was confirmed by X-ray diffraction and is presented in Figure 5. A comparison of selected metrical parameters for 2-Me2 and analogues bearing iodide and cyanide ligands has been compiled in Table 1. The octahedral geometry and structural features of the three congeners are quite similar; however, the modestly shortened Co(1)-C(5) bond length for



Figure 5. Molecular structure of $2-Me_2$ with 30% ellipsoids. Hydrogen atoms have been removed for clarity.

Table 1. Comparison of Selected Bond Distances (Å) and
Angles (deg) for cis,mer-(PMe ₃) ₃ Co(CH ₃) ₂ X (X = O'	Γf, I,
CN)	

	OTf	I ^a	CN^b	
Co(1)-C(1)	2.038(3)	2.033(10)	2.062(5)	
Co(1) - C(5)	2.008(3)	2.038(7)	2.054(5)	
Co(1)-P(1)	2.238(2)	2.249(2)	2.207(2)	
Co(1)-P(2)	2.292(2)	2.263(3)	2.229(5)	
Co(1)-P(3)	2.234(2)	2.237(2)	2.205(1)	
P(1)-Co(1)-P(3)	163.51(4)	166.45(10)	162.07(5)	
C(1)-Co(1)-P(2)	168.25(9)	167.9(3)	167.47(11)	
C(5)-Co(1)-X	175.3(1)	172.9(4)	179.0(2)	
^{<i>a</i>} Reference 16. ^{<i>b</i>} Reference 17.				

 $2-Me_2$ demonstrates the weaker *trans* influence of the triflate ligand compared to iodide and cyanide.

More significant to mechanistic considerations, the absence of isotopic crossover upon addition of MeOTf to $1-d_6Me_2$ coupled with the successful preparation of 2-Me₂ from $(PMe_3)_4CoCH_3$ indicates that path B is likely not operative for methyl group exchange. As depicted in Figure 4, methyl iodide reductive elimination from the cobalt(III) dimethyl species would generate (PMe₃)₃CoCH₃, which must be formed in low concentrations, as it remains undetected during the experiment and is reported to be unstable in the absence of additional phosphine.²⁰ The alternative synthesis of $2-Me_2$ (eq 2) from methyl triflate and $(PMe_3)_4CoCH_3$ occurs much faster than bimetallic methyl group exchange and likely proceeds via reaction of MeOTf with transiently generated, four-coordinate (PMe₃)₃CoCH₃. Under these conditions the concentration of MeOTf is high relative to (PMe₃)₃CoCH₃ and should thus provide a rapid trap for the unobserved (PMe₃)₃CoCH₃ to yield significant isotopic incorporation into the dimethyl cobalt triflate product if path B were operable. In addition, reactions between the more stable four-coordinate cobalt(I) species (PMe₃)₃CoI (1) and methyl iodide produced a mixture of products including 1-Me₂, (PMe₃)₃CoI₂, and insoluble cobalt material. Finally, the likelihood of a second-order process requiring two cobalt intermediates of very low concentration also augers poorly for path B.

Path C: Cobalt(I)-Catalyzed Disproportionation. The reversible disproportionation of transition metal-methyl ligands has recently been highlighted in palladium systems as a possible intermediate step for methane homologation and oxidatively induced C-C bond elimination.² Analogous disproportionation events from $1-Me_2$ could account for the intermolecular methyl exchange (eq 3), but would require

$$2(PMe_3)_3Co^{II}(CH_3)_2I$$

$$\approx (PMe_3)_3Co^{II}(CH_3)I + (PMe_3)_2Co^{IV}(CH_3)_3I$$

$$+ PMe_3$$
(3)

formation of a rather uncommon organocobalt(IV) species and likely necessitate the loss of phosphine to avoid hypervalency.¹⁸ This equilibrium formation was deemed unlikely for $1-Me_2$ given the unusual oxidation state for organocobalt and an absence of accelerated scrambling at higher cobalt concentrations (*vida infra*). Alternatively, a cobalt(I)-catalyzed disproportionation–comproportionation sequence could affect the same net exchange of methyl ligands via the more common



Figure 6. Cobalt(I)-catalyzed pathway for methyl group exchange.



Figure 7. Bimetallic iodide dissociation pathway for methyl group exchange.



Figure 8. Bimetallic phosphine dissociation pathway for methyl group exchange.

3+, 2+, and 1+ oxidation states of cobalt (Figure 6; path C).¹⁹ In path C, a trace quantity of tris(trimethylphosphine)cobalt(I) halide, formed by reductive elimination of $1-Me_2$ or persisting from the synthesis of $1-Me_2$,^{3,20} comproportionates with $1-d_3Me_2$ to transiently afford two isotopologues of tris(trimethylphosphine)cobalt(II) methyl halide. A productive reversion of this step would disproportionate a pair of matched cobalt(II) centers to yield $1-Me_2$ and $1-d_6Me_2$ as well as regenerate the cobalt(I) catalyst. However, the viability of the cobalt(I)-catalyzed pathway was easily discounted by intentional addition of (PMe₃)₃CoI and (PMe₃)₃CoCI to samples of $1-d_3Me_2$, which afforded no observed acceleration in intermetallic exchange.

Path D: lodide Loss-Bimetallic Exchange. The failure to detect methyl group ejection from 1-Me₂ as either a methyl radical or methyl cation equivalent in earlier experiments implies that alkyl ligand exchange most likely occurs via formation of a dicobalt intermediate or transition structure. Since 1-Me₂ is an electronically saturated complex, formation of such a bimetallic structure would probably require loss of at least one ligand (either I⁻ or PMe₃) from the coordination sphere. While the reversible loss of PMe₃ from 1-Me₂ has previously been implicated as a step preceding reductive ethane elimination, loss of the halide ligand would generate a more electrophilic cobalt cation complex.³ In addition, use of polar solvents with 1-Me2 and related cobalt complexes has demonstrated the potential lability of the Co-I bond and in some cases resulted in substitution of the iodide with the solvent (e.g., acetonitrile).²¹ The enhanced electrophilicity of the cation could then facilitate formation of a transient bridging methyl structure (Figure 7; path D). In this path dissociation of an iodide ligand would afford a 16-electron cationic intermediate, which is trapped by a second equivalent of 1 d_3Me_2 acting as a nucleophile in a concerted interchange substitution-type transition structure.²²

A direct method to examine path D is the inhibition of crossover by added iodide salts such as (${}^{n}Bu_{4}N$)I. Unfortunately, this salt has only modest solubility in arene solvent, and the use of more polar coordinating solvents could block path D by saturating the cationic intermediate. After testing the stability of **1-Me**₂ at ambient temperature in a variety of poorly coordinating polar solvents, chlorobenzene was selected as the most suitable solvent for testing iodide inhibition.²³ Interestingly, addition of 5 equiv of (${}^{n}Bu_{4}N$)I to C₆D₅Cl solutions of 1- d_3Me_2 produced no detectable inhibition in the formation of 1-Me₂ compared to parallel samples without the iodide source over two days at ambient temperature. This observation is difficult to reconcile with methyl exchange occurring via path D.

Path E: Phosphine Loss–Bimetallic Exchange. An alternative bimetallic route for methyl ligand exchange is the loss of PMe₃ from $1-Me_2$ to obtain a neutral five-coordinate cobalt species (Figure 8; path E). Similar to path D, a coordinately unsaturated intermediate would exchange the cobalt–methyl positions by forming a transient bridging alkyl structure. An analogous mechanism has previously been implicated in the cobalt-to-cobalt methyl group exchange at cyclopentadienyl cobalt dimethyl phosphine complexes studied by Bergman and co-workers (eq 4).^{1a}

 $CpCo(CH_3)_2PPh_3 + CpCo(CD_3)_2PPh_3 \longrightarrow 2 CpCo(CD_3)(CH_3)PPh_3$ (4)

In this elegant work, the authors employed labeling studies, ligand inhibition experiments, and the simulation of experimental reaction kinetics to detect and study the crossover reaction.

On the basis of the previous studies by Bergman and the prior observation of reversible PMe₃ loss from $1-Me_{22}^{3}$

examinations of path E were in fact among the first mechanistic experiments our laboratory performed on this system. Given the similarities in structure and cobalt oxidation state, it seemed reasonable to expect a resemblance between the exchange pathways for 1-Me₂ and CpCoMe₂PPh₃. Yet as mentioned briefly in an earlier report, preliminary experiments monitoring the conversion of $1-d_3Me_2$ to $1-Me_2$ by ¹H NMR spectroscopy with 10-20 equiv of free PMe₃ revealed no significant inhibition of exchange compared to parallel NMR tube samples without added PMe₃.³ Having then proceeded to examine and discount a range of alternative pathways for intermolecular methyl group exchange as described above, our mechanistic studies appeared frustrated. However, upon repeating the PMe₃ inhibition experiments over longer time courses, a significant observation was made. Monitoring the scrambling of $1-d_3Me_2$ in the presence of excess PMe₃ over three days at ambient temperature appeared to produce nonequilibrium quantities of $1-Me_2$ (i.e., a greater than 25% conversion to $1-Me_2$). This suggested that additional 1-Me2 may be formed by incorporating $-CH_3$ groups from a source other than the cobalt-methyl sites and that such a process could mask PMe3 inhibition of intermetallic exchange when solely ¹H NMR spectroscopy was used to quantify methyl transfer.

Reversible P–CH₃ Bond Cleavage. The only significant source for additional proton incorporation into the tris-(trimethylphosphine)cobalt dimethyl iodide species was PMe₃, as these reactions were performed in deuterated solvents under anhydrous conditions. Additionally, only d_0 , d_3 , and d_6 isotopologues of ethane (from reductive elimination) and **1**-**Me**₂ were observed during the experiment, indicating that any scrambling process involving PMe₃ must occur via P–C cleavage as opposed a C–H bond activation. Cleavage of P–C bonds at transition metals is fairly common for aryl-substituted phosphines,²⁴ but significantly more rare for phosphorus–alkyl bonds.²⁵

The activation of trimethylphosphine was confirmed by addition of 10 equiv of PMe₃ to a sample of $1-d_6Me_2$ (eq 5),



which resulted in formation of $1-d_3Me_2$, $1-Me_2$, and PMe_3-d_3 (detected by GC-MS) at ambient temperature over two days. It is important to consider that while exchange of a methyl substituent between phosphine and cobalt is evident, this process does not account for the substantial formation of $1-d_6Me_2$ and/or C_2D_6 observed in previous crossover and reductive elimination experiments using $1-d_3Me_2$. Instead two separate pathways for cobalt–methyl isotopic exchange appear operative: an intermetallic exchange of the Co–CH₃ groups and reversible P–CH₃ bond cleavage. In order to gain perspective on the relative rates of these two reactions, a

parallel NMR tube study was conducted. One NMR tube was charged only with $1-d_6Me_2$, while a second sample contained an equimolar mixture of $1-d_6Me_2$ and $1-Me_2$, holding the total cobalt concentration the same for both samples. Over one day at ambient temperature the first sample (which may exchange only by PMe₃ activation) exhibited only trace formation of $1-d_3Me_2$, while the second tube contained more than one-third $1-d_3Me_2$. This demonstrates that under identical conditions and without added phosphine the intermetallic exchange of the Co-CH₃ ligands is dramatically faster than exchange from reversible P-CH₃ cleavage.

The effect of free PMe₃ on P-CH₃ cleavage was further explored by monitoring the conversion of $1-d_6Me_2$ to $1-d_3Me_2$ and 1-Me₂ with varying amounts of added phosphine (eq 5). Samples with excess PMe₃ (4–10 equiv) produced mixtures of $1-d_3Me_2$ and $1-Me_2$ at considerably higher conversions (20-35) times greater) than parallel samples without additional phosphine. The dependence of reversible P-CH₃ cleavage on the concentration of free PMe₃ suggests that the activation does not occur via a classical P-C bond oxidative addition reaction as was observed by Wolczanski, Andersen, Wakatsuki, and others with earlier transition metals.²⁵ A possible mechanism consistent with the limited data in hand is nucleophilic attack of outer-sphere PMe₃ on a Co-CH₃ bond to reversibly form a cobalt phosphorane intermediate (Figure 9).²⁶ Similar metallophosphorane complexes have been widely implicated in the scrambling of ligand alkyl/aryl groups during palladiumcatalyzed cross-coupling reactions, though these typcially form via an intramolecular nucleophilic reaction between phosphine and alkyl/aryl ligands.^{24b}

Reexamination of Path E. The evidence of two significant routes for conversion of $1-d_3Me_2$ to $1-Me_2$ in the presence of excess PMe₃ complicates the endeavor to detect inhibition of intermetallic methyl group exchange by added phosphine and through these experiments provides evidence for the mechanism in Figure 8 (path E). Alternative attempts to inhibit methyl group exchange using other phosphine donors were inconclusive, as these reactions produced either other cobalt species (e.g., PPh₃) or no measurable effect for sterically hindered ligands (e.g., PCy₃). Additionally, attempts to establish a second-order dependence on the concentration of the cobalt complex showed little change between samples with increasing metal concentrations. However this does not strictly exclude path E if the initial phosphine dissociation is rate limiting under the conditions of the experiment. Thus a new investigation was pursued using a chelating phosphine with steric and electronic effects similar to PMe₃.

A tridentate analogue of trimethylphosphine MeP- $(CH_2CH_2PMe_2)_2$ (triphos) was prepared by the coupling of dimethyl phosphine and divinylmethyl phosphine similar to the procedure previously described by King and Cloyd.²⁷ The strong chelate effect of this ligand should dramatically slow the rate of cobalt-to-cobalt methyl transfer relative to PMe₃ if path E is operative. In order to test this hypothesis, the synthesis of



Figure 9. Possible pathway for methyl group exchange between PMe₃ and 1-Me₂.

(triphos)Co(CH₃)₂I was attempted by addition of the tridentate ligand to $1-Me_2$, a method our laboratory has previously used to good effect in installing bidentate ligands for other studies. However, upon stirring the reactants in diethyl ether for 18 h, a light yellow precipitate was formed, which has been tentatively assigned as two isomers of the cationic [(triphos)Co(CH₃)₂PMe₃]I complex (eq 6). This product



mixture was sparingly soluble in benzene- d_6 and exhibited three Co-CH₃ resonances in the ¹H NMR spectrum. Notably, one Co-CH₃ resonance at -0.05 ppm exhibited an apparent 10-line splitting pattern derived from ³ J_{P-H} coupling, indicating the presence of more than three phosphorus nuclei. Additional evidence that the isolated products resulted from iodide dissociation was obtained from analogous experiments treating the triflate complex **2-Me**₂ with triphos ligand to produce samples with identical NMR spectra to those originating from **1-Me**₂.

The mechanism of the cationic $[(triphos)Co(CH_3)_2PMe_3]I$ formation was not examined experimentally, but is likely to begin via substitution between a triphos -PMe2 group and the PMe₃ of 1-Me₂ bound trans to Co-CH₃ (this PMe₃ site has proven the most labile in previous EXSY NMR studies).³ Such a sequence could lead to a circumstance where the last triphos phosphine group to bind is positioned opposite the remaining Co-PMe3 bond, affording preferential substitution of the iodide over PMe3. If this is true, use of a more strongly bound halide could slow anion dissociation, permit more time for geometric rearrangements, and allow formation of the desired neutral (triphos) $Co(CH_3)_2X$ (X = halide) species. Fortunately, stirring the chloride congener cis,mer-(PMe₃)₃Co(CH₃)₂Cl (3-⁸ with triphos in tetrahydrofuran over one day did indeed $Me_2)^2$ afford good yields of *cis,mer*-(triphos)Co(CH₃)₂Cl (4-Me₂) (eq 7). Small quantities of the corresponding cationic product were



also observed in the reaction, but were easily removed by filtration from hydrocarbon solvent. Complex **4-Me**₂ was prepared only in small quantities and characterized by oneand two-dimensional NMR analysis. The ¹H NMR spectrum of **4-Me**₂ exhibited signals for the two Co–CH₃ sites at –0.98 (dt) and 1.22 (td) ppm. Significantly, two of the three resonances for the PMe_n ligands appeared as virtual triplets in the ¹H NMR spectrum, indicating a *trans* orientation of the triphos –PMe₂ groups and establishing a meridional coordination for the chelate. Control experiments monitoring equimolar mixtures of 3-Me₂ and 3- d_6 Me₂ at ambient temperature were performed first and established that the chloride-substituted PMe₃ complex undergoes intermetallic methyl transfer, easily observable by NMR spectroscopy after 4–6 h, comparable to the time scale for the iodide analogue.²⁹ More significantly, parallel NMR studies indicated that the mixtures of PMe₃-bound 3-Me₂ and 3- d_6 Me₂ exchanged methyl groups dramatically faster than samples of triphos-bound 4-Me₂ and 4- d_6 Me₂ (Figure 10).



Figure 10. Comparison of methyl group exchange processes between PMe₃- and triphos-supported cobalt(III) dimethyl chloride complexes.

After 36 h the trimethylphosphine species had reached an equilibrium ratio (1:2) of 3-Me₂ to $3-d_3Me_2$, as judged by ¹H NMR spectroscopy, while the triphos complexes had achieved minimal exchange with a 1:0.4 ratio of $4-Me_2$ to $4-d_3Me_2$. This observation is consistent with requisite phosphine dissociation during cobalt-to-cobalt methyl group exchange and strongly supports proposed path E as the intermetallic methyl exchange mechanism. Additionally, crossover experiments between 4- Me_2 and $3-d_6Me_2$ showed substantial exchange over the 36 h period. In this case, the formation of 4-d₃Me₂ and 3-d₃Me₂ was evident within 4 h of mixing, dramatically faster than the 24 h required to observe $4-d_3Me_2$ by NMR spectroscopy in the triphos self-exchange experiment. This qualitative difference in exchange rate suggests that only one of the two cobalt centers must achieve coordinative unsaturation in order for exchange to occur (Figure 11) and provides additional evidence for proposed path E.

CONCLUDING REMARKS

Having investigated multiple plausible mechanisms for cobaltto-cobalt methyl group exchange in cis,mer-(PMe₃)₃Co- $(CH_3)_2X$, the available evidence most strongly supports a route where phosphine dissociation at one cobalt center is followed by attachment to a second equivalent of cobalt(III) dimethyl halide to transiently form a high-energy dicobalt structure with bridging methyl groups (Figure 8; path E). The dissociation of the bridging methyl structure could then produce a net exchange of the labeled alkyl groups. This mechanism is supported by relative isotopic exchange rates and crossover experiments with PMe3- and triphos-supported 3-Me₂ and 4-Me₂. Multiple plausible alternative pathways for intermetallic exchange, including radical crossover, reversible methyl halide elimination, and cobalt(I)-catalyzed disproportionation, were also considered but excluded on the basis of trapping tests, isotopic labeling studies, and other comparative rate experiments. During the course of these mechanistic investigations, a second phosphine-dependent methyl exchange reaction was revealed to swap -CH₃ substituents between



Figure 11. Crossover methyl group exchange between $4-Me_2$ and $3-d_6Me_2$.



Figure 12. Partial reaction pathway for ethane reductive elimination from 1-Me₂.

cobalt and PMe₃. This second exchange reaction complicates some mechanistic probes of the cobalt-to-cobalt exchange, but occurs with negligible rates in the absence of added PMe₃. The preliminary data are consistent with $P-CH_3$ scission proceeding through reversible PMe₃ nucleophilic attack on a cobalt-methyl group to produce a transient cobalt phosphorane intermediate.

The two pathways for methyl group exchange at cobalt are each influenced by the presence of free phosphine, as is the rate of reductive ethane elimination from 1-Me₂ (Figure 12), which was the focus of earlier studies that led to the investigations described here. The methyl exchange process between cobalt and phosphine is unlikely to impact the rate of C-C bond reductive elimination from cobalt(III), as the two reactions are observable only under essentially mutually exclusive concentrations of free PMe₃. Conversely, ethane elimination from 1-Me₂ and the cobalt-to-cobalt methyl group exchange appear to share a common unobserved intermediate, $(PMe_3)_2Co(CH_3)_2I_1$ which means intermetallic methyl exchange could in principle influence the rate and mechanistic investigations of reductive eliminations from cobalt(III) species. However the cobalt-tocobalt methyl exchange proceeds on a time scale far faster than C-C bond coupling, takes place without any other detectable intermediates, and is a degenerate reaction that only reproduces the reactants (though isotoptically scrambled if the species are labeled). These features indicate that the intermetallic methyl exchange reactions observed in cobalt(III) dimethyl halide complexes are unlikely to have meaningful impacts on the kinetics of C-C bond reductive elimination from the species, which our laboratory is pursuing as part of ongoing efforts to elucidate the pathways and influencing factors for selective C-C bond formation at base metal centers.

EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out using standard vacuum, Schlenk, cannula, or glovebox techniques. Compounds $1-Me_2$, ¹⁶ $3-Me_2$, ²⁸ (PMe_3)₄CoCH₃, ²⁰ and MeP-(CH₂CH₂PMe₂)₂²⁷ were prepared according to previously described procedures. All other chemicals were purchased from Aldrich, VWR, Strem, or Cambridge Isotope Laboratories. Volatile chemicals were dried with 4 Å molecular sieves and distilled prior to use. Solvents were dried and deoxygenated using literature procedures.³⁰

¹H, ²H, ¹³C, ¹⁹F, and ³¹P NMR spectra were recorded on Bruker DRX 400 Avance and 300 Avance MHz spectrometers. ¹H and ¹³C chemical shifts are referenced to residual protio solvent signals; ³¹P and ¹⁹F chemical shifts are referenced to an external standard of H_3PO_4 and trifluorotoluene, respectively. Probe temperatures were

calibrated using ethylene glycol and methanol as previously described.¹⁵ IR spectra were recorded on Jasco 4100 FTIR or Metler Toledo React IR spectrometers. X-ray crystallographic data were collected on Bruker Smart Apex I or D8 Quest diffractometers. The structures were solved from direct methods and Fourier syntheses and refined by full-matrix least-squares procedures with anisotropic thermal parameters for all non-hydrogen atoms. Crystallographic calculations were carried out using SHELXTL. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Ledgewood, NJ, or Atlantic Microlab, Inc., in Norcross, GA (USA).

Preparation of *cis,mer*-(PMe₃)₃Co(CH₃)₂(SO₃CF₃) (2-Me₂). *Method A.* A 50 mL Schlenk flask was charged with 0.092 g (0.24 mmol) of (PMe₃)₄Co(CH₃) and approximately 10 mL of diethyl ether. On a high-vacuum line, 2 equiv (89 Torr in 101 mL; 0.49 mmol) of MeOTf was transferred into the Schlenk flask at -196 °C via calibrated gas bulb. The reaction mixture was then stirred at ambient temperature for two hours. The reaction mixture was cannula filtered into a new Schlenk flask to remove a dark precipitate. The resulting orange solution was evaporated to afford 35 mg (31%) of 2-Me₂ as an orange powder. This compound can be recrystallized from diethyl ether at -35 °C. Similar procedures performed in a J. Young tube indicate near quantitative conversion by NMR spectroscopy, suggesting the modest isolated yield may be due to decomposition of 2-Me₂ during workup. Attempts to perform the synthesis in the absence of light did not dramatically improve the yield.

Method B. A J. Young NMR tube was charge with 0.007g (0.019 mmol) of 1-Me₂ and approximately 400 μ L of benzene- d_6 . On a highvacuum line, 1 equiv (27 Torr in 10.9 mL; 0.019 mmol) of MeOTf was added at -196 °C via calibrated gas bulb. Full conversion of 1-Me₂ to (PMe₃)₃Co(CH₃)₂OTf and MeI was observed by ¹H NMR spectroscopy in less than one hour at ambient temperature. Anal. Calcd for C12H33F3O3P3SCo: C 30.91; H 7.13. Found: C 30.81; H 6.84. ¹H NMR (23 °C; toluene- d_8): δ –1.57 (bs, 9.6 Hz, 3H, Co-CH₃), 0.67 (brs, 3H, Co-CH₃); 1.05 (brs, 27H, P-CH₃). ³¹P{¹H} NMR (23 °C; toluene- d_8): δ –7.71 (brs, 1P), 6.19 (brs, 2P). ¹⁹F NMR (23 °C; C₆D₆): δ –79.07. ¹H NMR (-40 °C, toluene-d₈): δ –1.65 (dt, 9.6 Hz, 9.5 Hz, 3H, Co-CH₃), 0.72 (brt, 3H, Co-CH₃); 0.96 (d, 6.5 Hz, 9H, P-CH₃), 1.03 (vt, 3.0 Hz, 18H, P-CH₃). ³¹P{¹H} NMR (–40 °C; toluene- d_8): δ –5.95 (t, 27.9 Hz, 1P), 9.09 (d, 27.9 Hz, 2P). ¹³C{¹H} NMR (-40 °C; toluene- d_8): δ -22.80 (Co-CH₃), 3.43 (Co-CH₃), 12.96 (P-CH₃), 15.89 (P-CH₃), 120.13 (CF₃, ${}^{1}J_{CF} = 320.3$ Hz). IR (KBr): $\nu_{O=S=O} = 1299 \text{ cm}^{-1}$

Preparation of *cis,mer*-[MeP(CH₂CH₂PMe₂)₂]Co(CH₃)₂(Cl) (4-Me₂). A 20 mL scintillation vial was charged with 0.064 g (0.181 mmol) of 3-Me₂, 0.041 g (0.183 mmol) of MeP(CH₂CH₂PMe₂)₂, and approximately 5 mL of tetrahydrofuran. The solution was stirred at ambient temperature for approximately one day. Three times during this period, the solvent and free trimethylphosphine were removed *in vacuo* followed by redissolving the reaction mixture in tetrahydrofuran. After one day the solvent was removed and the residue extracted using pentane and diethyl ether to yield 50 mg (83%) of 4-Me₂ as an orange

powder when dried under vacuum. Complex **4-Me**₂ is rather lipophilic and requires hours of drying under vacuum at room temperature to obtain powdered samples from solution. Elemental analysis was not obtained for this species due to the small scale of synthesis, which was necessitated by safety concerns in generating dimethyl phosphine for the preparation of MeP(CH₂CH₂PMe₂)₂. A description of safe synthetic procedures for this ligand has been reported by King and Cloyd.²⁷ ¹H NMR (C₆D₆): δ –0.98 (dt, 8.4 Hz, 7.9 Hz, 3H, Co-CH₃), 0.67 (d, 7.2 Hz, 3H, P-CH₃), 0.85 (vt, 3.4 Hz, 6H, P-CH₃), 1.22 (td, 8.0 Hz, 3.6 Hz, 3H, Co-CH₃), 1.26–1.43 (m, 4H, PCH₂), 1.51 (vt, 4.1 Hz, 6H, P-CH₃), 2.08–2.46 (m, 4H, PCH₂). ³¹P{¹H} NMR (C₆D₆): δ 50.41 (br, 2P), 111.40 (br, 1P). ¹³C{¹H} NMR (C₆D₆): δ –13.43 (Co-CH₃), -0.58 (Co-CH₃), 10.86 (P-CH₃), 11.64 (P-CH₃), 12.26 (P-CH₃), 24.81 (PCH₂), 33.77 (PCH₂).

General Procedure for Monitoring Bimetallic Methyl Group Exchange by ¹H NMR Spectroscopy. In a typical experiment a J. Young NMR tube(s) was charged with a stock solution of $1-d_3Me_2$ in benzene- d_6 (0.015-0.020 M). The sample(s) was then allowed to stand at ambient temperature. At intervals the sample(s) was inserted into a 400 MHz NMR probe, and ³¹P decoupled ¹H NMR spectra were acquired. The ratio of $1-d_3Me_2$ and $1-Me_2$ was determined by integration of singlet resonances at -0.743 (1-Me₂) and -0.759 ppm $(1-d_3Me_2)$. When possible, samples were cooled to 10 °C to obtain sharper line shapes and better separation of the peaks for the two isotopologues. Analogous procedures can be used for monitoring exchange between $1-Me_2$ and $1-d_6Me_2$ using equimolar solutions. This method was also employed to study exchange in 3-Me₂ and 4-Me₂ isotopologues. Relative rates of isotopic exchange were always monitored using parallel NMR tube samples to obviate variations in temperature, mixing, or exposure to ambient light (which produced modest accelerations in isotopic exchange).

ASSOCIATED CONTENT

S Supporting Information

Crystal Information File for $2-Me_2$ and $3-Me_2$ and NMR spectrum of $4-Me_2$. These data are available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: wb36@brown.edu.

Notes

The authors declare no competing financial interest.

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