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Mechanistic Considerations for C−C Bond Reductive Coupling at a Cobalt(III) Center

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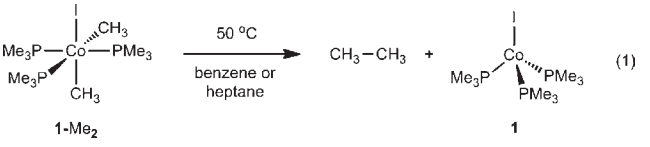
Supporting Information

ABSTRACT: The diamagnetic cobalt(III) dimethyl complex, *cis,mer*-$(PMe_3)_3Co(CH_3)_2I$, was found to promote selective C−C bond formation, affording ethane and triplet $(PMe_3)_3CoI$. The mechanism of reductive elimination has been investigated by a series of kinetic and isotopic-labeling experiments. Ethane formation proceeds with a rate constant of $3.1(5) \times 10^{-5}$ s^{-1} (50 °C) and activation parameters of $\Delta H^{\ddagger}$ = 31.4(8) kcal/mol and $\Delta S^{\ddagger}$ = 17(3) eu. Addition of free trimethylphosphine or coordinating solvent strongly inhibits reductive elimination, indicating reversible phosphine dissociation prior to C−C bond-coupling. EXSY NMR analysis established a rate constant of 9(2) s^{-1} for phosphine loss from *cis,mer*-$(PMe_3)_3Co(CH_3)_2I$. Radical trapping, crossover, and isotope effect experiments were consistent with a proposed mechanism for ethane extrusion where formation of an unobserved five-coordinate intermediate is followed by concerted C−C bond formation. An unusual intermolecular exchange of cobalt−methyl ligands was also observed by isotopic labeling.

Transition metal-mediated carbon−carbon bond-forming reactions have been at the forefront of synthetic method development for more than five decades.[1] The broad impact of this methodology has spurred efforts to expand the scope of transition metal catalysts for C−C bond cross-coupling and other transformations beyond the successful but expensive platinum group metals.[2] Accordingly, economical and less toxic first-row transition metal sources have become targets of growing interest.[2] Many exciting examples of base-metal-promoted carbon−carbon coupling reactions have been reported and suggest that the key bond-forming step(s) may occur via a range of redox pathways including ligand-centered, combined metal−ligand, and metal-centered net two-electron reductive elimination reactions.[3] In addition, these transformations at base metals may easily traverse between open- and closed-shell spin systems.[2] By contrast, the carbon−carbon bond-forming reductive elimination process in precious metal cross-coupling reactions is believed to proceed primarily through metal-centered, two-electron redox events which have been implicated in many elegant mechanistic studies.[4]

The mechanistic models for C−C bond elimination which have guided catalysis at precious metals have received considerably more investigation than their lighter first-row metal congeners.[4] The limited range of isolable base-metal complexes which undergo selective, stoichiometric carbon−carbon bond reductive elimination may account for the modest scope of mechanistic study.[5] The relative weakness of first-row transition metal−carbon bonds, the frequent presence of alternative β-hydride elimination routes, and the exceptional thermal and air sensitivity of many base-metal hydrocarbyl complexes are just some origins of this dearth of examples. These factors have been of particular hindrance to the study of difficult $C_{sp^3}-C_{sp^3}$ bond formations. However, in the 1970s, Yamamoto and Ikariya reported a series of investigations into the thermal decomposition of dialkylcobalt(III) complexes supported by phosphine and acetylacetonato (acac) ligands.[6] Among the reactions studied, a rare example of selective ethane reductive elimination from cobalt(III) was described for *cis*-$(PhPMe_2)_2(acac)Co(CH_3)_2$.[6c] Unfortunately, the alkane elimination occurred with degradation of the presumed cobalt(I) product, obviating further mechanistic study.[6c] Inspired by these observations, as well as the recent advances in the use of cobalt as a C−C bond cross-coupling catalyst,[7] our laboratory began a study into the mechanism for metal-centered, two-electron C−C bond elimination at strong field cobalt complexes.

Given the significant challenges associated with deciphering between the multiple possible redox pathways available to base metals in C−C bond reductive elimination reactions and the rarity of selective hydrocarbyl eliminations from cobalt centers, our initial investigations were directed toward cobalt species likely to undergo solely metal-based redox changes.[2,5] The conveniently prepared dialkyl cobalt complex, *cis,mer*-$(PMe_3)_3Co(CH_3)_2I$ (**1-Me$_2$**),[8] has proven a useful platform for detailed study of this class of transformation.



1-Me$_2$ 1 (1)

The strong-field, redox-innocent phosphine and methyl ligands afford a diamagnetic complex which is reasonably stable in hydrocarbon or ethereal solvents. Although **1-Me$_2$** was first characterized by Klein and Karsch in 1975,[9] little has been reported regarding its reactivity. Our laboratory observed that **1-Me$_2$** completes a smooth reductive elimination of ethane at 50 °C in benzene or heptane solutions over the course of hours (eq 1). Significantly, the reaction afforded a stable cobalt(I) triplet species, $(PMe_3)_3CoI$ (**1**),[10] and no detectable quantity of methane by ^{1}H NMR spectroscopy. The selective ethane elimination suggests that **1-Me$_2$** circumvents deleterious radical extrusion pathways in preference for a net two-electron C−C bond coupling. This attribute, along with the modest pace of elimination and relative stability of the cobalt product, provided

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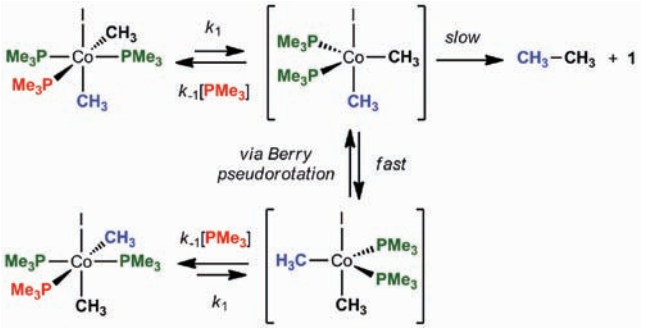

Figure 1. Reversible PMe_3 dissociation prior to ethane loss.

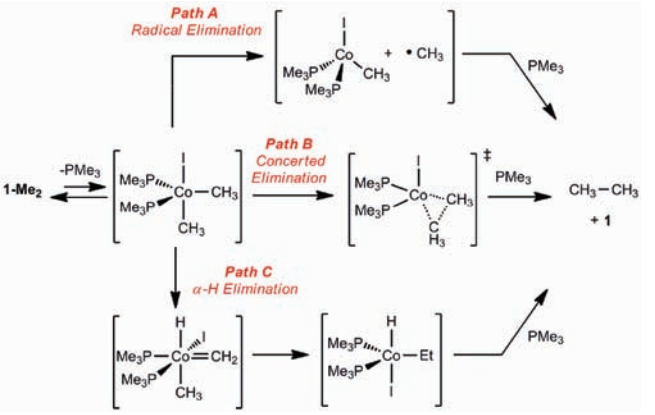

Figure 2. Possible paths for ethane elimination from **1-Me$_2$**.

an unusual opportunity to gain insight into the kinetics and mechanism of C−C bond formation at strong-field cobalt(III) centers.

Reductive ethane elimination from octahedral complexes has substantial precedent in late transition metals, although most examples occur at second- and third-row metals.[4,11] There has been significant interest in determining whether these heavier metal complexes extrude alkanes via a direct reductive elimination from a coordinatively saturated species or proceed with dissociation of a ligand to eliminate from a lower coordinate intermediate.[4] In order to investigate the potential role of ligand dissociation in C−C bond coupling at cobalt, the influence of added phosphine on **1-Me$_2$** was examined by a series of kinetic experiments. Ethane elimination from **1-Me$_2$** in benzene-d_6 solution was monitored by ^{1}H NMR spectroscopy at 50 °C over three half-lives and afforded a rate constant of $3.1(5) \times 10^{-5}$ s^{-1}. The observed rate constant was confirmed by independent measurement of $2.4(7) \times 10^{-5}$ s^{-1} (50 °C) using UV−vis spectrophotometry and the method of initial rates.[12] These rates correspond to a barrier of ca. 25 kcal/mol and are within a range commonly observed for ethane elimination from d^6-octhedral complexes.[4a,j,11] Attempts to monitor ethane elimination from **1-Me$_2$** in the presence of 2 equiv of free PMe_3 failed to produce detectable alkane formation over 3 days at 50 °C. Thermolysis at temperatures in excess of 90 °C resulted in slow decomposition into an intractable mixture. Thermolysis of **1-Me$_2$** in coordinating solvent (acetonitrile-d_3) also failed to produce reductive elimination at elevated temperatures.[13] Notably, addition of excess ^{n}Bu$_4$NI yielded no significant change in the rate of ethane extrusion (within the saturation limit of the salt in benzene). The dramatic inhibition of C−C bond coupling by added PMe_3 and donor solvent is consistent with a pre-dissociation pathway for elimination, and implicates formation of an unobserved five-coordinate intermediate prior to ethane loss (Figure 1). The role of phosphine loss from cobalt as a rate influencing event in reductive elimination motivated further investigation into the ligand dissociation process.

EXSY NMR spectra of **1-Me$_2$** with 2 equiv of added PMe_3 (mixing time 150 ms; 27 °C) exhibited strong exchange correlations between free phosphine and the PMe_3 ligand bound *trans* to methyl, as well as between the two Co−CH_3 sites. A rate of PMe_3 dissociation from **1-Me$_2$** (k_1; Figure 1) of 9(2) s^{-1} was determined by quantitative EXSY NMR analysis over multiple mixing times with a free PMe_3 concentration of 0.053 M.[13] Significantly, the rate of phosphine loss is dramatically faster than the overall rate of ethane elimination ($3.1(5) \times 10^{-5}$ s^{-1}), even accounting for the variation in temperature between the measurements. This confirms that loss of PMe_3 from **1-Me$_2$** to access a coordinatively unsaturated complex is not rate limiting, and the C−C bond formation likely represents the slowest event in the elimination reaction.

Methyl−methyl site exchange in **1-Me$_2$** was similarly analyzed in the 2D EXSY NMR spectra and found to occur with a rate constant of 6.9(7) s^{-1} (27 °C). Significantly, this rate is indistinguishable from the measured rate of PMe_3 loss from **1-Me$_2$** (9(2) s^{-1}) and was found to be independent of the concentration of added phosphine (up to 0.5 M free PMe_3). The precision of methyl site exchange rate measurements were considerably greater than those for free/bound PMe_3 exchange, owing to the superior signal dispersion of the methyl resonances and the ability to record EXSY NMR spectra in the absence of added phoshine.[13] The interchange of the two Co−CH_3 sites was monitored over a 45 °C range and established activation parameters of $\Delta H^{\ddagger}$ = 23(2) kcal/mol and $\Delta S^{\ddagger}$ = 21(6) eu. The absence of [PMe_3] dependence and the substantially favorable entropy of activation are consistent with a site exchange pathway where dissociation of PMe_3 from **1-Me$_2$** is rate limiting and followed by fast Berry pseudorotation[14] to exchange the two methyl ligands (Figure 1). Notably, the mechanism in Figure 1 does not require interchange of the Co-PMe_3 sites and is consistent with the selectivity of PMe_3 loss from **1-Me$_2$**. Although methyl−methyl site exchange in **1-Me$_2$** bears little direct influence on the rate or mechanism of ethane formation, the Eyring parameters for this process can be taken as a measure of the activation parameters for phosphine dissociation from **1-Me$_2$** as PMe_3 loss appears rate limiting for the intramolecular site exchange.

Investigations into the kinetics of PMe_3 exchange with **1-Me$_2$** provide a convincing case for the presence of a five-coordinate intermediate in route to ethane reductive elimination. However, greater insight into the mechanism of the C−C bond forming event itself was pursued. There are at least three possible pathways for C−C bond reductive elimination at strong field cobalt which could begin with PMe_3 loss (Figure 2).[4] In path A, the five-coordinate intermediate undergoes cobalt−methyl bond cleavage to form a methyl radical which could then either abstract a methyl group from the resulting cobalt(II) complex or recombine with another methyl radical.[15] Path B invokes concerted C−C bond formation, likely proceeding via a three-centered transition structure en route to ethane loss.[4d−k] Finally, path C would proceed through a sequence including α-hydride

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elimination, methyl migratory insertion into a methylidene, and C−H bond reductive elimination.[4a,b] Each pathway would likely finish with rapid scavenging of the free phosphine by a low-coordinate cobalt complex to generate **1**. Significantly, an inter-system crossing event is required at some point along each mechanism to account for conversion of diamagnetic **1-Me$_2$** to the $S = 1$ cobalt(I) monoiodide species. Definitive determination of when this spin-state change occurs is not possible with the experimental data in hand; however, it is plausible that the crossing event occurs subsequent to the loss of the strong-field methyl ligand(s).

These mechanistic pathways were examined by kinetic and isotopic-labeling experiments beginning with the α-hydride elimination/methyl migratory insertion route (path C). This mode of C−C bond formation has previously found only limited experimental support for alkane elimination at late transition metals[4a,b,16] and was excluded for **1-Me$_2$** on the basis of isotope effects of 1.2(2) (by NMR) and 1.3(1) (by UV−vis) at 50 °C for **1-Me$_2$**/**1-d_6Me$_2$** (**1-d_6Me$_2$** = *cis,mer*-$(PMe_3)_3Co(CD_3)_2I$).[13] An isotope effect of this magnitude is inconsistent with the substantially larger effect anticipated for a reaction pathway which involves breaking a C−H/D bond during α-hydride elimination and forming a C−H/D bond in ethane reductive elimination,[17] even if a modest inverse equilibrium isotope effect is incurred for a slow alkane dissociation event.[18] In addition, the absence of observable quantities of methane or ethylene which could form from transient cobalt(III) methyl methylidene hydride and cobalt(III) ethyl hydride species, respectively, argues against path C as the mechanism of ethane formation.

Radical (path A) and concerted (path B) mechanisms both have considerable precedents for C−C bond coupling at late transition metals and were regarded as probable pathways for ethane extrusion.[4d−k,15] Initial investigations of these pathways included monitoring the rate of reductive elimination over a 46 °C range which afforded Eyring parameters of $\Delta H^{\ddagger} = 31.4(8)$ kcal/mol and $\Delta S^{\ddagger} = 17(3)$ eu.[13] However, this favorable entropy of activation could be consistent with either methyl radical extrusion from **1-Me$_2$** (path A) or a late, highly dissociative transition state for concerted C−C bond elimination (path B). Therefore, detection of a free methyl radical intermediate during elimination was attempted using 1,4-cyclohexadiene (CHD) as a trapping agent.[19] Thermolysis of **1-Me$_2$** in the presence of 5 equiv of CHD (ca. 0.25 M) yielded less than 8% methane as the alkane product, suggesting the presence of an outer-sphere methyl radical intermediate was minimal. Still, the observation of small quantities of methane does not completely rule out contributions from a tightly caged radical or rapid radical rebound version of path A, which can be difficult to confirm experimentally.[20] These observations motivated additional study of the radical pathway by crossover experiments.

In order to monitor the origins of the two methyl fragments in the ethane product, the *cis,mer*-$(PMe_3)_3Co(CD_3)(CH_3)I$ (**1-d_3Me$_2$**) isotopologue was prepared. Consistent with the observation of rapid site exchange between methyl ligands, **1-d_3Me$_2$** appeared as an essentially equimolar mixture of two isotopomers by ^{1}H NMR spectroscopy. Thermolysis of **1-d_3Me$_2$** at 60 °C for 3 h yielded complete conversion to a mixture of CH_3CH_3, CD_3CH_3, and CD_3CD_3, with a 1:4 ratio of CH_3CH_3 to CD_3CH_3 (Figure 3). Moreover, careful monitoring of the reaction at lower conversions revealed more selective formation of CD_3CH_3 at short reaction times (1:9 at ca. 15% conv) with a drop in selectivity occurring over the course of the reaction. Both the deviation from a 1:2:1 statistical distribution of product

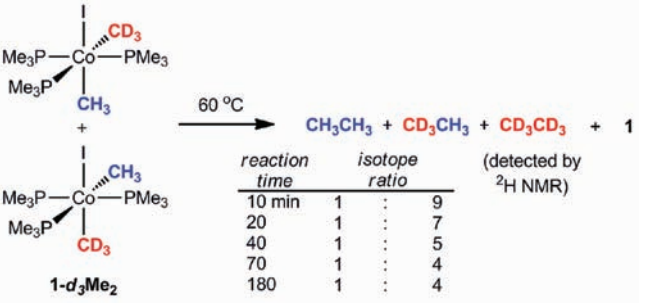

Figure 3. Elimination crossover from **1-d_3Me$_3$**.

isotopologues and the change in ratio over the reaction are inconsistent with a standard outer-sphere radical mechanism for ethane elimination (path A).

The result of radical-trapping and crossover experiments auger poorly for outer-sphere versions of path A. However, the observation of crossover in the ethane product is also inconsistent with a straightforward concerted pathway (path B) without an explanation for the origins of CH_3CH_3 and CD_3CD_3. Note that the intramolecular methyl−methyl site exchange described for **1-Me$_2$** would not result in crossover from **1-d_3Me$_2$**, and given the selective formation of only three isotopologues of ethane, the crossover event is unlikely to involve C−H bond cleavage. Isotopic scrambling following reductive elimination was excluded by thermolysis of **1-Me$_2$** in the presence of CD_3CD_3, which yielded no detectable CD_3CH_3 product. Closer examination of phosphorus-decoupled ^{1}H NMR spectra of **1-d_3Me$_2$** at low conversion revealed two new Co−CH_3 signals shifted slightly downfield from those of **1-d_3Me$_2$**.[13] The new signals were attributed to formation of **1-Me$_2$** prior to reductive elimination, and the assignment was confirmed by independently mixing samples of **1-Me$_2$** and **1-d_3Me$_2$**. The small change in Co−CH_3 resonances of the two isotopologues is ascribed to an isotopic perturbation of the chemical shifts.[21] This observation confirms that the apparent crossover from **1-d_3Me$_2$** is in fact a result of intermolecular methyl group exchange prior to ethane elimination[22] and renders concerted elimination (path B) as the most likely of the considered pathways for ethane formation. The mechanism of intermolecular methyl group exchange remains the subject of investigation but does not appear to be intimately linked to reductive elimination. Preliminary experiments indicate that the degree of intermolecular exchange is not inversely related to [PMe_3] or coordinating solvent (conditions which obviate ethane formation). Further examination of the mechanism for this process is ongoing.

In conclusion, selective reductive elimination of ethane from a dimethylcobalt(III) complex has been observed with preliminary mechanistic studies indicating a pathway where dissociation of a phosphine ligand precedes a largely concerted C−C bond formation. This mechanistic model provides a rare comparison to the more intensely studied platinum group metal reductive elimination reactions and may assist in developing base-metal alternatives for processes now dominated by precious or toxic metals. Commonalities between the pathway of elimination from **1-Me$_2$** and the most commonly espoused mechanisms for C−C bond-coupling at precious metals are likely a result of the strong-field ligands supporting **1-Me$_2$**. However, the observation of intermolecular methyl group exchange, the necessity of a spin-state change during the reaction of **1-Me$_2$**, and the

precedent for single-electron events in many other organocobalt complexes offer intriguing deviations from the typical heavier metal congeners. Efforts to identify the role the of the intersystem crossing event and to extend this avenue of study to weaker field or redox-variable platforms are current research targets which should provide further insight into key base-metal-promoted transformations.

■ ASSOCIATED CONTENT

Supporting Information. Full experimental details, sample rate measurements, Eyring plots, and selected NMR and UV−vis spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) (a) Brandsma, S. F.; Vasilevsky, H. D. *Applications of Transition Metal Catalysis in Organic Synthesis*; Springer: London, 1998. (b) Miyaura, N. *Cross-Coupling Reactions: A Practical Guide*; Springer-Verlag: Berlin, 2002.

(2) (a) Chirik, P. J.; Wieghardt, K. *Science* **2010**, *327*, 794. (b) Bullock, M. R. *Catalysis Without Precious Metals*; Wiley-VCH: Weinheim, 2010.

(3) For examples of recent reviews: (a) Bolm, C. *Nat. Chem.* **2009**, *1*, 420. (b) Cahiez, G.; Moyeux, A. *Chem. Rev.* **2010**, *110*, 1435. (c) Jana, R.; Pathak, T. P.; Sigman, M. S. *Chem. Rev.* **2011**, *111*, 1417. (d) Lin, S.; Agapie, T. *Synlett* **2011**, 1.

(4) (a) Byers, P. K.; Canty, A. J.; Crespo, M.; Puddephatt, R. J.; Scott, J. D. *Organometallics* **1988**, *7*, 1363. (b) de Graff, W.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1989**, *8*, 2907. (c) Williams, B. S.; Goldberg, K. I. *J. Am. Chem. Soc.* **2001**, *123*, 2576. (d) Hill, G. S.; Puddephatt, R. J. *Organometallics* **1998**, *17*, 1478. (e) Espinet, P.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 4707. (f) Arthur, K. L.; Wang, Q. L.; Bregel, D. M.; Smythe, N. A.; Williams, S. B.; Goldberg, K. I. *Inorg. Chem.* **2005**, *44*, 7732. (g) Gatard, S.; Celeligil-Cetin, R.; Guo, C.; Foxman, B. M.; Ozerov, O. V. *J. Am. Chem. Soc.* **2006**, *128*, 2808. (h) Hartwig, J. F. *Inorg. Chem.* **2007**, *46*, 1936. (i) Madison, B. L.; Thyme, S. B.; Keene, S.; Williams, B. S. *J. Am. Chem. Soc.* **2007**, *129*, 9538. (j) Ghosh, R.; Emge, T. J.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2008**, *130*, 11317. (k) Racowski, J. M.; Dick, A. R.; Sanford, M. S. *J. Am. Chem. Soc.* **2009**, *131*, 10974.

(5) (a) Huffman, W. L.; Kochi, J. K. *Organometallics* **1982**, *1*, 155. and references therein. (b) Hill, D. H.; Parvez, M. A.; Sen, A. *J. Am. Chem. Soc.* **1994**, *116*, 2889. (c) Sherry, B. D.; Fuerstner, A. *Acc. Chem. Res.* **2008**, *41*, 1500. (d) Enthaler, S.; Junge, K.; Beller, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 3317.

(6) (a) Ikariya, T.; Yamamoto, A. *Chem. Let.* **1976**, 85. (b) Ikariya, T.; Nakamura, Y.; Yamamoto, A. *J. Organomet. Chem.* **1976**, *118*, 101. (c) Yamamoto, A.; Ikariya, T. *J. Organomet. Chem.* **1976**, *120*, 257.

(7) (a) Hess, W.; Treutwein, J.; Hilt, G. *Synthesis* **2008**, *22*, 3537. (b) Smith, A. L.; Hardcastle, K. I.; Soper, J. D. *J. Am. Chem. Soc.* **2010**, *132*, 14358. (c) Cahiez, G.; Moyeux, A. *Chem. Rev.* **2010**, *110*, 1435.

(8) Beck, R.; Klein, H. F. *Z. Anorg. Allg. Chem.* **2008**, *634*, 1971.

(9) (a) Klein, H. F.; Karsch, H. H. *Chem. Ber.* **1975**, *108*, 944. (b) Klein, H. F.; Karsch, H. H. *Chem. Ber.* **1975**, *108*, 956.

(10) Klein, H. F.; Karsch, H. H. *Inorg. Chem.* **1975**, *14*, 473.

(11) (a) Crumpton, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2000**, *122*, 962. (b) Kloek, S. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2007**, *129*, 3460.

(12) (a) Hall, K. J.; Quickenden, T. I.; Watts, D. W. *J. Chem. Educ.* **1976**, *53*, 493. (b) Casado, J.; Lopez-Quintela, M. A.; Lorenzo-Barral, F. M. *J. Chem. Educ.* **1986**, *63*, 451.

(13) See Supporting Information.

(14) (a) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933. (b) Ugi, L.; Marquarding, D. P.; Klusacer, H.; Gillespie, P. *Acc. Chem. Res.* **1971**, *4*, 288. (c) Couzijn, E. P.A; Slootweg, J. C.; Ehlers, A. W.; Lammertsma, K. *J. Am. Chem. Soc.* **2010**, *132*, 18127.

(15) (a) Hager, E.; Sivaramakrishna, A.; Clayton, H. S.; Mogorosi, M. M.; Moss, J. R. *Coord. Chem. Rev.* **2008**, *252*, 1668. (b) Khusnutdinova, J. R.; Rath, N. P.; Mirica, L. M. *J. Am. Chem. Soc.* **2010**, *132*, 7303. (c) Hojilla Atienza, C. C.; Milsmann, C.; Lobkovsky, E.; Chirik, P. J. *Angew. Chem. Int. Ed* **2011**, *50*, 8143–8147.

(16) Fryzuk, M. D.; Gao, X.; Joshi, K.; MacNeil, P. *J. Am. Chem. Soc.* **1993**, *115*, 10581.

(17) Schrock, R. R. In *Reactions of Coordinated Ligands*; Braterman, P. R., Ed.; Plenum: New York, 1986.

(18) Parkin, G. *Acc. Chem. Res.* **2009**, *42*, 315.

(19) Hawari, J. A.; Engel, P. S.; Griller, D. *Int. J. Chem. Kin.* **1985**, *17*, 1215.

(20) (a) Braden, D. A.; Parrack, E. E.; Tyler, D. R. *Coord. Chem. Rev.* **2001**, *211*, 279. (b) Hlavica, P. *Eur. J. Biochem.* **2004**, *271*, 4335.

(21) Berger, S. *NMR: Basic Princ. Prog.* **1990**, *22*, 1.

(22) (a) Hill, G. S.; Yap, G. P. A.; Puddephatt, R. J. *Organometallics* **1999**, *18*, 1408. (b) Remy, M. S.; Cundari, T. R.; Sanford, M. S. *Organometallics* **2010**, *29*, 1522.