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Reductively induced homolytic carbon–carbon bond cleavage in Co(CO)$_3$(PPh$_3$)(COCF$_3$)

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Abstract

The chemical or electrochemical reduction of the trifluoroacetyl complex Co(CO)$_3$(PPh$_3$)(COCF$_3$) involves a single electron transfer yielding trifluoromethyl radical and an anionic cobalt carbonyl complex. The mechanism is proposed to involve electron transfer followed by initial dissociation of either a carbonyl or phosphine ligand from the 19-electron [Co(CO)$_3$(PPh$_3$)(COCF$_3$)]$^-$ anion. The resulting 17-electron intermediate undergoes subsequent one-electron reductive elimination of trifluoromethyl radical by homolytic cleavage of the carbon–carbon bond of the trifluoroacetyl group. The CF$_3^{\cdot}$ radical can be trapped by either benzophenone anion, forming the anion of α-(trifluoromethyl)benzhydrol, or Bu$_3$SnH, yielding CF$_3$H. The ultimate organometallic product is an 18-electron anion, either [Co(CO)$_4$]$^-$ or [Co(CO)$_3$(PPh$_3$)]$^-$, depending upon which ligand is initially lost. Fluorine-containing products were identified and quantitated by ^{19}F NMR while cobalt-containing products were determined by IR.
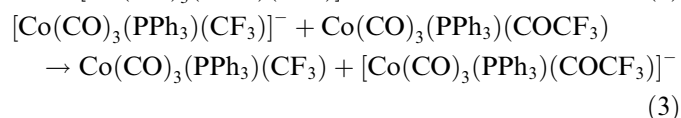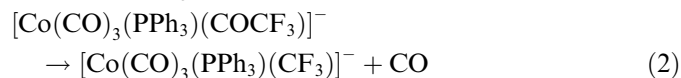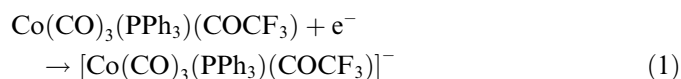© 2007 Elsevier B.V. All rights reserved.

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1. Introduction

We have had a long-standing interest in the reactivity of odd-electron organotransition metal complexes produced by redox reactions, and in particular those reactions which are catalytic with respect to electrons (electron transfer chain catalysis or ETC [1]). Recently, we have been studying the reduction of the trifluoroacetylcobalt complex Co(CO)$_3$(PPh$_3$)(COCF$_3$) (1). This particular complex is one of the most thermally stable cobalt acyl complexes [2] and the trifluoromethyl group provides a convenient NMR label for following reactivity. While several examples of oxidatively and reductively induced migratory insertion reactions have been reported [3–7], so far as we are aware there are no examples of redox initiated decarbonylation reactions other than that of one rhenium formyl complex [8]. Though perfluoroalkyl ligands are considered unlikely

to participate in migratory insertion of CO because of their relatively strong metal–carbon bonds [9], we felt that compound **1** was a good candidate for the reverse. The fact that the thermal decarbonylation of **1** is slow makes it possible to investigate the initiation and catalysis of this reaction by electron transfer. The reduction of the related manganese compound, Mn(CO)$_5$(COCF$_3$), has been reported to occur at significantly less negative potentials than that of the corresponding trifluoromethyl complex, Mn(CO)$_5$CF$_3$ [10]. If the same held true for compound **1**, then it should be capable of participating in an electron transfer chain catalyzed decarbonylation reaction as follows:

$$Co(CO)_3(PPh_3)(COCF_3) + e^-$$
$$\rightarrow [Co(CO)_3(PPh_3)(COCF_3)]^- \quad (1)$$
$$[Co(CO)_3(PPh_3)(COCF_3)]^-$$
$$\rightarrow [Co(CO)_3(PPh_3)(CF_3)]^- + CO \quad (2)$$
$$[Co(CO)_3(PPh_3)(CF_3)]^- + Co(CO)_3(PPh_3)(COCF_3)$$
$$\rightarrow Co(CO)_3(PPh_3)(CF_3) + [Co(CO)_3(PPh_3)(COCF_3)]^-$$
$$(3)$$

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Initiation by reduction in Eq. (1) would be followed by a catalytic cycle consisting of Eqs. (2) and (3). While this particular application of ETC might not be exceptionally useful given the ease of thermal decarbonylation of compound **1** at elevated temperatures, the proof of concept would be significant.

Unfortunately, preliminary studies of the reduction of compound **1** failed to show any evidence for the proposed ETC decarbonylation reaction. Denisovich et al. have proposed that reduction of the Mn trifluoroacetyl complex yields, at least initially, the $[Mn(CO)_5]^-$ anion and trifluoroacetyl radical [10]. Since we observed metal carbonyl anions in the products from both the chemical and electrochemical reduction of compound **1**, we spent some time searching for products derived from the trifluoroacetyl radical, but also without success. On the other hand, Cordaro and Bergman have reported that the thermal decomposition of electron-rich trifluoroacetyl iridium compounds yields trifluoromethyl anion through heterolytic cleavage of the carbon–carbon bond of the trifluoroacetyl group [9c]. While we did observe CF_3H and CF_3D among the products of the reduction of compound **1** in deuterated solvents, other evidence, including the electron stoichiometry, argued against the production of trifluoromethyl anion. We have ultimately determined that the organic fragment being produced by reduction of **1** is trifluoromethyl radical. Below we will present evidence that reduction of compound **1** proceeds through a 19e$^-$ anionic intermediate which, after ligand dissociation, undergoes homolytic carbon–carbon bond cleavage in the trifluoroacetyl group. The cobalt-containing products have been identified and quantitated by infrared spectroscopy and the organic products by ^{19}F NMR.

2. Experimental

2.1. Reagents

$Co_2(CO)_8$ was obtained from Strem Chemicals and was used to synthesize $Co(CO)_3(PPh_3)(COCF_3)$ [11] and $Co_2(CO)_6(PPh_3)_2$ [12] by published procedures. Decamethylchromocene (DMC) was also obtained from Strem Chemicals. Stock solutions of the $[Co(CO)_4]^-$ and $[Co(CO)_3(PPh_3)]^-$ anions in 1:1 THF/CH$_3$CN were prepared by reduction of the cobalt carbonyl dimers with 1% Na(Hg). Solutions of K_2BP (potassium salt of benzophenone dianion [15]) were prepared by reaction of benzophenone in THF with an excess of K metal and were standardized by reaction with aqueous ethanol followed by titration with standardized HCl. Solutions of KBP (potassium salt of benzophenone anion) were prepared by 1:1 dilution of K_2BP with a THF solution of excess benzophenone and were also standardized with HCl. The THF was dried with CaH_2 and then distilled under nitrogen from sodium benzophenone anion before use. CH$_3$CN was distilled from CaH_2 under nitrogen. The supporting electrolyte for electrochemical experiments, $[Bu_4N]PF_6$,

was obtained from Alfa Aesar and was dried at 100 °C under vacuum before use. All other reagents were obtained commercially and were used as received. All chemical reactions were carried out in a nitrogen-atmosphere glove box.

2.2. Instrumentation

NMR spectra were acquired on either a Bruker DPX 300 or a Varian VNMRS 500. Proton chemical shifts were referenced to residual protons in the solvent, ^{19}F chemical shifts to external CFCl$_3$, and ^{31}P chemical shifts to external 85% H_3PO_4. IR spectra were obtained using a Mattson Instruments Genesis II FTIR and a cell with CaF_2 windows separated by a 0.1 mm spacer. Cyclic voltammetry was performed with a Bioanalytical Systems BAS 100B/W electrochemical analyzer using a 0.5 mm Pt disc working electrode, Pt wire auxiliary electrode, and Ag wire quasi-reference electrode. Solutions contained approximately 0.1 M $[Bu_4N]PF_6$ supporting electrolyte. All potentials are expressed relative to the formal potential of the ferrocenium–ferrocene couple (Fc^+/Fc).

3. Results and discussion

3.1. Electrochemistry of *1*

Fig. 1 shows the cyclic voltammogram of compound **1** in CH$_3$CN. It displays a single chemically irreversible reduction at -2.43 V vs. Fc^+/Fc. On the reverse scan, two anodic peaks are seen at -0.64 and -0.27 V, corresponding to the oxidation of products formed by the chemical reaction which follows the forward electron transfer. By comparison with authentic samples and with literature values [13], these anodic peaks were assigned to $[Co(CO)_3(PPh_3)]^-$
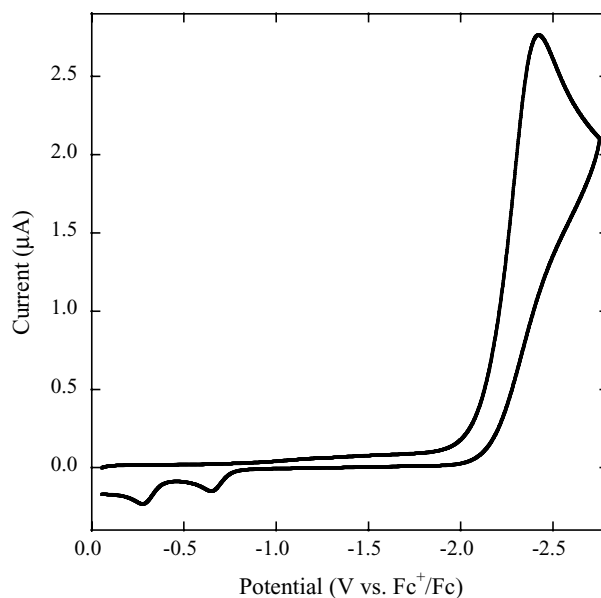

Fig. 1. Cyclic voltammogram of 3×10^{-3} M $Co(CO)_3(PPh_3)(COCF_3)$ in CH$_3$CN/$[Bu_4N]PF_6$ (0.1 M) at a Pt disc electrode at 0.2 V s^{-1}.

and $[Co(CO)_4]^-$, respectively. Comparison of the peak current for the reduction of compound **1** with that of the one-electron reduction of tris(dibenzoylmethanato)iron and the two-electron reduction of $[CpFe(CO)_2]_2$ at the same concentration indicates that the reduction of compound **1** is a one-electron process. Note that the relatively small sizes of the cobalt anion peaks on the reverse scan of the cyclic voltammogram are as would be expected for oxidations so far separated from the corresponding reduction on the forward scan and are therefore not to be taken as evidence for low yields of the anions. This effect is similar to that observed for chemically reversible but electrochemically irreversible redox couples in cyclic voltammetry [14]. The cyclic voltammetric behavior of **1** in THF is essentially the same as that in CH_3CN.

3.2. Chemical reduction of 1

The chemical reduction of compound **1** was performed in both CH_3CN and THF using either solutions of KBP or K_2BP in THF ($E^{0'} \approx -2.5$ V) or solid DMC ($E^{0'} \approx -1.6$ V) as the reducing agent. Note that DMC is likely able to reduce compound **1** despite its relatively low redox potential because the rapid chemical reactions of **1** shift the redox equilibrium toward the products. The IR spectrum of the product solution in CH_3CN showed carbonyl stretching bands at 1926, 1891, 1837, and 1695 cm^{-1}, while in THF bands were observed at 1926, 1886, and 1846 cm^{-1}. The bands at 1926 and 1837 cm^{-1} correspond to independently synthesized $K[Co(CO)_3(PPh_3)]$ and the one at 1891 cm^{-1} to $K[Co(CO)_4]$, both in CH_3CN. The relatively weak band observed at 1695 cm^{-1} in CH_3CN could not be identified, but is in the range reported for bridging carbonyl ligands on anionic cobalt carbonyl clusters [16]. Similar results have been obtained in controlled potential electrolyses of compound **1** [17].

In order to quantitatively account for the cobalt-containing products of the reduction of compound **1**, series of standard solutions of $K[Co(CO)_3(PPh_3)]$ and $K[Co(CO)_4]$ were prepared in 1:1 THF/CH_3CN. Plots of absorbance as a function of concentration at 1837 and 1891 cm^{-1}, respectively, were used to estimate the concentrations of the cobalt carbonyl anions in the mixture produced by the reduction of 10 mM **1** in CH_3CN using K_2BP in THF. The mixed solvent system was used for the calibration curves in order to most closely model the solution resulting from the chemical reduction of compound **1**. This analysis showed that the product solution contained 3.2 mM $K[Co(CO)_4]$ and 4.8 mM $K[Co(CO)_3(PPh_3)]$, accounting for 80% of the cobalt from the starting material. The production of these two anions in similar amounts agrees well with the cyclic voltammetry results. The missing cobalt may be accounted for by either precipitation of organometallic anions or the formation of higher nuclearity cobalt cluster anions as evidenced by the unassigned band at 1695 cm^{-1}.

The fate of the trifluoroacetyl group was determined by performing the reaction in d_8-THF and monitoring ^{19}F

NMR spectra. An internal standard of α,α,α-trifluorotoluene was used to quantitate the fraction of the original fluorine atoms accounted for by each observed product. In all experiments, greater than 90% of the starting material's fluorine atoms were accounted for in the product solution by comparison with the internal standard. Table 1 lists the results of these experiments, showing the relative percentage yield of each product as determined by integration of the ^{19}F NMR signals. Some decarbonylation to $Co(CO)_3(PPh_3)(CF_3)$, either thermally or perhaps via ETC, occurred but typically no more than 5% of the starting material was converted to this product. Using either K_2BP or KBP as reductant, approximately 20–30% of the fluorine-containing products consisted of a mixture of CF_3D (1:1:1 triplet at −79.0 ppm) and CF_3H (doublet at −78.3 ppm). Most of the fluorine, 70–80%, showed up initially in the ^{19}F NMR spectrum as a very broad peak centered at −74.7 ppm. Addition of a small amount of water converted this peak to a sharp singlet at the same chemical shift. The ^{31}P NMR spectrum showed a small quartet for the decarbonylation product at 52.2 ppm and singlets for triphenylphosphine (−5.4 ppm) and triphenylphosphine oxide (26.0 ppm). The triphenylphosphine oxide peak was minimized by careful drying of the solvent with molecular sieves, demonstrating that it most likely originated from a reaction involving hydroxide produced by reaction of traces of water with the reducing agent. No attempt was made to quantitate the yields of phosphorus-containing products.

The production of CF_3H and CF_3D could be accounted for by either deprotonation of solvent and/or trace water by CF_3^- anion or by hydrogen abstraction by $CF_3^\cdot$ radical. Unfortunately, because of the strongly reducing conditions of the reaction, we could not use CH_3OD as solvent to distinguish between these two possibilities as others have done [9c,18]. A survey of the literature on the reactivity of CF_3^- anion revealed that it can react with benzophenone to produce the anion of α-(trifluoromethyl)benzhydrol [19]. The reported ^{19}F NMR chemical shift of −74.5 ppm matches our value extremely well, and additionally we have obtained a commercial sample of the benzhydrol which gives the same NMR spectrum. Deprotonation of the commercial

Table 1
Percentage yields of products from the reduction of $Co(CO)_3(PPh_3)(COCF_3)$ in d_8-THF

Reductant Radical Trap[a]	K_2BP	KBP	KBP Bu₃SnH	DMC	DMC Bu₃SnH
CF_3H	18	25	58	10	78
CF_3D	0	2	0	24	0
$[Ph_2C(O)CF_3]^-$	80	66	37	0	0
$Co(CO)_3(PPh_3)(CF_3)$	2	3	0	4	0
Unassigned	0	3[b]	6[c]	62[d]	22[d]

[a] 10 equiv. vs. **1**.
[b] $\delta_{19F} = -83.1$ (s).
[c] $\delta_{19F} = -84.1$ (s), −76.9 (s).
[d] $\delta_{19F} = -74.1$ (s), −73.4 (s).

sample of α-(trifluoromethyl)benzhydrol with butyl-lithium also produces the same peak broadening that we observe in our initial product solutions. Thus the initially broad resonance for α-(trifluoromethyl)benzhydrol likely stems from proton exchange of the alkoxide, an effect which has been previously reported for the anion of α-(trifluorom-ethyl)benzyl alcohol [20]. Upon further reflection, we realized that there were two possible routes to the benzhydrol product when using either K_2BP or KBP as the reducing agent. Reaction of CF_3^- anion with benzophenone, Eq. (4), or reaction of $CF_3^{\cdot}$ radical with benzophenone anion, Eq. (5), would yield the same product.

$$CF_3^- + Ph_2CO \rightarrow [Ph_2C(O)CF_3]^- \qquad (4)$$

$$CF_3^{\cdot} + Ph_2CO^{\cdot -} \rightarrow [Ph_2C(O)CF_3]^- \qquad (5)$$
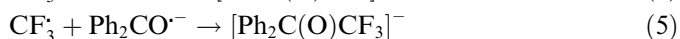
In fact, using K_2BP as the reducing agent would make the second reaction quite likely if $CF_3^{\cdot}$ were formed quickly following the electron transfer. Using KBP as reductant yielded the same ambiguous result, though with a somewhat lower yield of the benzhydrol anion.

We then decided to try to test for the intermediacy of $CF_3^{\cdot}$ by adding a hydrogen atom donor. The usual radical traps with benzylic hydrogens did not significantly affect the yield of CF_3H when **1** was reduced in d_8-THF. However, the literature indicates that while $CF_3^{\cdot}$ is highly reactive as a hydrogen atom abstractor, it strongly prefers hydrogens bound to less electronegative elements [21]. We therefore added 10 equiv. of Bu_3SnH as a radical trap and saw a large increase in the yield of CF_3H when using KBP as the reducing agent. In order to further differentiate between $CF_3^{\cdot}$ and CF_3^- and increase the yield of CF_3H, we performed the reduction of compound **1** using DMC as the reducing agent. In this case also, a very high yield of CF_3H was observed with Bu_3SnH compared with a much lower yield of a mixture of CF_3D and CF_3H in the absence of Bu_3SnH. This result conclusively identified $CF_3^{\cdot}$ radical as the organic intermediate produced by the chemical reactions following reduction of compound **1**.

One further piece of information determined via chemical reduction of compound **1** was the electron stoichiometry. Previous results from controlled potential electrolyses had agreed with cyclic voltammetric peak currents in indicating that the reduction of compound **1** is a net one-electron process [17]. This result was confirmed by titration of compound **1** using KBP and following the progress of the reaction by both IR (in THF) and NMR (in d_8-THF) spectroscopies. Though exact results were difficult to obtain, it consistently took slightly more than 1 equiv. (average of 1.3) of KBP to completely consume all of the starting material. An excess of KBP was most likely required because of reaction of $CF_3^{\cdot}$ with KBP. Using K_2BP the result was very close to one mole of K_2BP per mole of **1**. In this case it should be recognized that the reduction of compound **1** by K_2BP followed by reaction of $CF_3^{\cdot}$ radical with benzophenone anion, Eq. (5), amounts to a two-electron process, though only one of the electrons effects reduction of the cobalt complex. The other electron effectively reduces the

$CF_3^{\cdot}$. Therefore, based on the results of the chemical titrations of compound **1** with both KBP and K_2BP as well as cyclic voltammetry, we are confident that the reduction of **1** is a one-electron process.

3.3. Proposed mechanism for the reduction of compound 1

Scheme 1 shows the proposed mechanism for the reduction of compound **1**. The initial electron transfer produces an electron-rich $19e^-$ anion, $[Co(CO)_3(PPh_3)(COCF_3)]^-$. Like many $19e^-$ organometallic complexes, this species likely participates in rapid equilibration with $17e^-$ intermediates via dissociation of one of the ligands [22]. Based upon the relative yields of $[Co(CO)_4]^-$ and $[Co(CO)_3-(PPh_3)]^-$, it appears that dissociation of a CO ligand is slightly favored. Homolytic cleavage of the C–C bond of the trifluoroacetyl group converts the $17e^-$ anion to an $18e^-$ anion and $CF_3^{\cdot}$ radical in what is effectively a one-electron reductive elimination. An alternative mechanism would involve cleavage of the C–C bond prior to ligand dissociation, but this would generate a $20e^-$ organometallic intermediate and so is considered much less likely. Interestingly, comparison can be made between this reaction and previously reported oxidatively-induced one-electron reductive eliminations [23,24]. In order for a one-electron ligand to be lost directly from the metal following oxidation of an $18e^-$ compound, prior coordination of another two-electron ligand is required. Reductive elimination thus occurs from a $19e^-$ species. In the present case, the carbonyl group of the trifluoroacetyl ligand functions as the new two-electron ligand after dissociation of the $CF_3^{\cdot}$ radical and reductive elimination occurs from a $17e^-$ species.

Another alternative mechanism proposed by a reviewer of this manuscript is decarbonylation of the $17e^-$ intermediate anion followed by C–Co bond cleavage to yield the
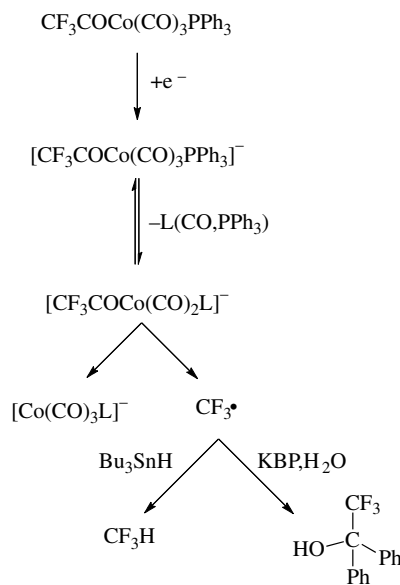
Scheme 1.

trifluoromethyl radical and anionic cobalt carbonyl complex. We have eliminated this possibility by examining the reduction of the trifluoromethyl complex, $Co(CO)_3$-$(PPh_3)(CF_3)$, synthesized by thermal decarbonylation of compound **1** [25]. Reduction of the trifluoromethyl complex with KBP yielded a mixture of anionic cobalt carbonyl complexes similar to that obtained with compound **1**, but only about a 5% yield of α-(trifluoromethyl)benzhydrol. Reduction of the trifluoromethyl complex in the presence of Bu_3SnH yielded less than 10% CF_3H. We therefore conclude that the reduction of compound **1** is unlikely to proceed through the anion of the trifluoromethyl complex as an intermediate. This conclusion is also consistent with the lack of ETC substitution which would otherwise be expected to occur if this anion were formed.

In CH_3CN only, an unassigned CO stretching band is observed in the product solution at 1695 cm^{-1}. It was originally suspected that this band originated from an organic product containing the trifluoroacetyl fragment. However, ^{19}F NMR spectroscopy accounts for essentially all of the fluorine in the starting material, so it now seems unlikely this IR band represents such an organic carbonyl compound. This frequency is consistent with that of bridging carbonyl ligands in some known anionic cobalt carbonyl clusters [15], and so we are tentatively assigning it to such a species. However, attempts to isolate this species for definitive characterization have not been successful.

4. Conclusions

The reduction of $Co(CO)_3(PPh_3)(COCF_3)$ does not lead to either dissociation or decarbonylation of the trifluoroacetyl ligand. Instead, dissociation of one of the neutral ligands, CO or PPh_3, occurs in order to decrease the electron count at cobalt in accordance with the 18-electron rule and the known reactivity of other 19e$^-$ species. It then appears that the resulting 17e$^-$ anion, $[Co(CO)_2(L)$-$(COCF_3)]^-$ (L = CO or PPh_3), undergoes homolytic carbon–carbon bond cleavage in the trifluoroacetyl group to yield trifluoromethyl radical and a stable 18e$^-$ anionic cobalt complex. This reaction amounts to a one-electron reductive elimination in which the oxidation state of the cobalt decreases from zero to negative one. Since both reductive elimination of trifluoromethyl radical and decarbonylation involve cleavage of the C–C bond of the trifluoroacetyl group, it appears that the lack of electron transfer catalyzed decarbonylation likely stems from a lack of favorable interaction between the CF_3^- radical and the 18e$^-$ cobalt center. The instability of such a F_3C–Co bond is also evidenced by the rapid decomposition of the trifluoromethyl complex upon reduction.

References

[1] (a) T.V. Magdesieva, K.P. Butin, Russ. Chem. Rev. 71 (2002) 223;
(b) M.-H. Delville, Inorg. Chim. Acta 291 (1999) 1;
(c) F. Battaglini, E.J. Calvo, F. Doctorovich, J. Organomet. Chem. 547 (1997) 1;
(d) D. Astruc, Angew. Chem., Int. Ed. Engl. 27 (1988) 643.
[2] R.F. Heck, J. Am. Chem. Soc. 85 (1963) 651.
[3] R.H. Magnuson, R. Meirowitz, S.J. Zulu, W.P. Giering, Organometallics 2 (1983) 460.
[4] A. Morneau, B.T. Donovan-Merkert, W.E. Geiger, Inorg. Chim. Acta 300–302 (2000) 96.
[5] C. Amatore, M. Bayachou, J.-N. Verpeaux, L. Pospisil, J. Fiedler, J. Electroanal. Chem. 387 (1995) 101.
[6] R.S. Bly, G.S. Silverman, M.M. Hossain, R.K. Sly, Organometallics 3 (1984) 642.
[7] D. Miholová, A.A. Vlek, J. Organomet. Chem. 240 (1982) 413.
[8] B.A. Narayanan, C. Amatore, C.P. Casey, J.K. Kochi, J. Am. Chem. Soc. 105 (1983) 6351.
[9] (a) H. Berke, R. Hoffmann, J. Am. Chem. Soc. 100 (1978) 7224;
(b) C.J. Bourgeois, R.P. Hughes, T.L. Husebo, J.M. Smith, I.M. Guzei, L.M. Liable-Sands, L.N. Zakharov, A.L. Rheingold, Organometallics 24 (2005) 6431;
(c) J.G. Cordaro, R.G. Bergman, J. Am. Chem. Soc. 126 (2004) 16912.
[10] L.I. Denisovich, M.G. Peterleitner, A.A. Stepanor, S.M. Peregudova, Russ. Chem. Bull. 49 (2000) 375.
[11] R.F. Heck, D.S. Breslow, J. Am. Chem. Soc. 84 (1962) 2499.
[12] A.R. Manning, J. Chem. Soc. (A) (1968) 1135.
[13] (a) Y. Zhen, W.G. Feighery, C.-K. Lai, J.D. Atwood, J. Am. Chem. Soc. 111 (1989) 7832;
(b) C.-K. Lai, W.G. Feighery, Y. Zhen, J.D. Atwood, Inorg. Chem. 28 (1989) 3929;
(c) K.Y. Lee, J.K. Kochi, Inorg. Chem. 28 (1989) 567.
[14] W.R. Heineman, P.T. Kissinger, in: P.T. Kissinger, W.R. Heineman (Eds.), Laboratory Techniques in Electroanalytical Chemistry, Marcel Dekker, New York, 1984, p. 92.
[15] T. Yoshimura, Z. Hou, Y. Wakatsuki, Organometallics 14 (1995) 5382.
[16] (a) P. Chini, V. Albano, J. Organomet. Chem. 15 (1968) 433;
(b) P. Chini, V. Albano, S. Martinengo, J. Organomet. Chem. 16 (1969) 471.
[17] (a) C.C. Wilkinson, B.S. Thesis, Baylor University, December 1999;
(b) Z. Lin, M.S. Thesis, Baylor University, December 2003.
[18] P.J. Toscano, H. Brand, S. Liu, J. Zubieta, Inorg. Chem. 29 (1990) 2101.
[19] G.K.S. Prakash, J. Hu, G.A. Olah, Org. Lett. 5 (2003) 3253.
[20] J. Russell, N. Roques, Tetrahedron 54 (1998) 13771.
[21] W.R. Dolbier Jr., Chem. Rev. 96 (1996) 1557.
[22] (a) S. Sun, D.A. Sweigart, Adv. Organomet. Chem. 40 (1996) 171;
(b) D.R. Tyler, Acc. Chem. Res. 24 (1991) 325;
(c) D. Astruc, Chem. Rev. 88 (1988) 1189.
[23] T. Aase, M. Tilset, V.D. Parker, J. Am. Chem. Soc. 112 (1990) 4974.
[24] J. Kim, S.L. Gipson, Polyhedron 23 (2004) 1371.
[25] W. Hieber, W. Beck, E. Lindner, Z. Naturforsch. Teil. B 16 (1961) 229.