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Reductive acceleration of the migratory insertion reaction: evidence that insertion occurs in a 19-electron intermediate

Bernadette T. Donovan, and William E. Geiger

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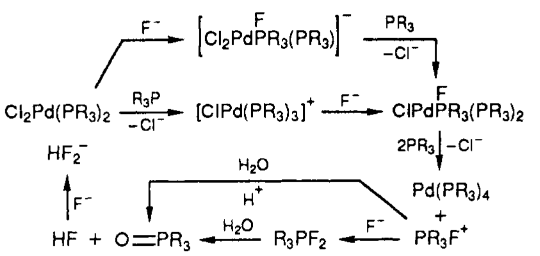
Scheme I



Moreover, reduction failed to take place when water was added to a mixture of PPh_3 and $PdCl_2$ but did occur when fluoride ion was added. The addition of less than a stoichiometric amount of fluoride results in only partial reaction, presumably owing to the formation of the exceedingly stable HF_2^- ion from the protons liberated in the reaction (Scheme I). Analysis of the filtrate of reaction 1 by ^{31}P NMR spectroscopy gave evidence for the formation of the phosphine monoxide $Ph_2P(CH_2)_3P(O)Ph_2$ (δ(^{31}P) 31.0, −17.2 ppm) as one of two observable oxidation products. The other bidentate phosphines employed also yielded the phosphine monoxides (and not the dioxides) as the final oxidation products. This assignment is unambiguous since $[Ph_2P(O)CH_2]_2$ and $[Ph_2P(O)]_2CH_2$ exhibit singlet ^{31}P NMR resonances, whereas the monoxides $Ph_2PCH_2P(O)Ph_2$ and $Ph_2P(CH_2)_2P(O)Ph_2$ each exhibit two doublets.[13] The filtrates of reaction mixtures of the type exemplified by reaction 1 also contained a difluorophosphorane product. For $(Ph_2PCH_2)_2$, $Ph_2PCH_2CH_2PF_2Ph_2$ was identified by comparison of its ^{31}P and ^{19}F NMR spectroscopic parameters[14] to those previously reported.[15] The difluorophosphorane products for the other ligands employed were similarly identified.[16,17]

A plausible reaction pathway is proposed in Scheme I. Nucleophilic attack of fluoride on phosphorus followed by transfer of two electrons from phosphorus to palladium yields the palladium(0) complex and a fluorophosphonium salt. Although we did not observe fluorophosphonium cations in this reaction, $[Ph_3PF]^+$ has been reported in the literature and it is known to react readily with fluoride in solution to give Ph_3PF_2,[18] which we have identified in our reaction solution. Hydrolysis of the difluorophosphorane to the phosphine oxide completes the scheme. Other pathways, such as prior coordination of fluoride to palladium followed by migration of the fluoride to phosphorus, cannot be ruled out.

We are presently investigating the scope of this reaction using other phosphorus ligands and additional metals, as well as the potential for making it catalytic in fluoride.

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[13] ^{31}P NMR (DMSO): $Ph_2PCH_2P(O)Ph_2$ δ 28.8 (d), −27.1 (d), $^2J_{P-P}$ = 50.5 Hz; $Ph_2PCH_2CH_2P(O)Ph_2$ δ 32.3 (d), −12.4 (d), $^3J_{P-P}$ = 47.3 Hz. For literature values see: (a) Grim, S. O.; Walton, E. D. *Inorg. Chem.* **1980**, *19*, 1982. (b) Berners-Price, S. J.; Johnson, R. K.; Mirabelli, C. K.; Faucette, L. F.; McCabe, F. L.; Sadler, P. J. *Inorg. Chem.* **1987**, *26*, 3383.

[14] ^{31}P NMR (DMSO): δ −12.4 (d, $^3J_{P-P}$ = 69 Hz), −40.5 (td, $^1J_{P-F}$ = 644 Hz). ^{19}F NMR (DMSO): δ 125.3 (d, $^1J_{P-F}$ = 644 Hz).

[15] Ruppert, I. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 662.

[16] NMR data (compound, $\delta(^{31}P^{III})$, $\delta(^{31}P^{V})$, $^1J_{P-F}$, $^nJ_{P-P}$, $\delta(^{19}F)$, $^3J_{P-F}$): $Ph_2PCH_2PF_2Ph_2$, −23.9 (dt), −41.9 (td), 643 Hz, 63.9 Hz, 136.1 (ddt), 22.5 Hz; $Ph_2P(CH_2)_3PF_2Ph_2$, −17.3 (s), −42.4 (t), 643 Hz, −125.8 (d); $Ph_2P(CH_2)_4PF_2Ph_2$, −15.6 (s), −40.8 (t), 639 Hz; $Ph_2PCH_2CMe_2CH_2PF_2Ph_2$, −23.6 (s), −44.4 (t), 657 Hz; Ph_3PF_2, −54.0 (t), 657 Hz.

[17] Ruppert, I.; Bastian, V. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 718.

[18] Seel, V. F.; Bassler, H. J. *Z. Anorg. Allg. Chem.* **1975**, *418*, 263.

Reductive Acceleration of the Migratory Insertion Reaction: Evidence That Insertion Occurs in a 19-Electron Intermediate

Bernadette T. Donovan and William E. Geiger*

Department of Chemistry
University of Vermont, Burlington, Vermont 05405

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Summary: The electrochemical reduction of the cobaltacycle $Cp(CO)CoC_{12}H_8$ (**1**) has been studied in tetrahydrofuran/0.1 M Bu_4NPF_6 by cyclic voltammetry, bulk coulometry, and rotating-ring-disk voltammetry. This complex reduces in an irreversible one-electron process at ca. −1.7 V vs SCE. Within the time frame of a CV scan, about $^1/_3$ equiv of the fluorenone anion, Fl^-, is produced per equiv of **1**$^-$. Since **1** produces Fl only slowly when heated under CO, it is clear that the reduction of **1** results in an enormous increase in the rate of alkyl to acyl migratory insertion for this complex. Since the insertion must occur immediately after uptake of an electron by **1**, a 19e intermediate is responsible for the enhanced rate of migratory insertion. A body of earlier work on redox acceleration of migratory insertion reactions has led to controversy over whether insertion occurs at the 17e or 19e stage. The present results offer definitive evidence that 19e species may show very large enhancements in their rates of migratory insertions.

Alkyl to acyl migratory insertion reactions are known to be enormously accelerated in odd-electron organometallic complexes.[1-4] However, there is controversy over whether the insertion step occurs in the 17-electron or 19-electron species.[2,5-7] With one exception,[7] redox acceleration of the reaction has been achieved by oxidation of an 18-electron complex in the presence of a nucleophile. Two routes may be envisioned for insertion after formation of the 17e species $[L_nM(CO)(CH_3)]^+$ (Scheme I), depending on whether migration occurs before coordination of Nu (in the 17e radical cation, top route) or after (in the 19e intermediate, bottom route). In spite of very careful experimentation, especially involving Cp(L)Fe(CO)Me (Cp = η^5-C_5H_5),[2,5,6b] no consensus exists on the mechanistic question.

We now report an example of rapid alkyl to acyl migratory insertion in which a 19e complex formed in the absence of an added ligand is the most reasonable structure to precede the insertion step.

The 18e cobaltacycle $Cp(CO)CoC_{12}H_8$[8] (**1**) simplifies the mechanistic possibilities because it is only labile at the Co–CO bond under our conditions.[9] Earlier work showed

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[1] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; p 373.

[2] Golovin, M. N.; Meirowitz, R.; Rahman, M. M.; Liu, H. Y.; Prock, A.; Giering, W. P. *Organometallics* **1987**, *6*, 2285 and references therein.

[3] Sheridan, J. B.; Han, S.-H.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1987**, *109*, 8097.

[4] Gipson, S. L.; Kneten, K. *Inorg. Chim. Acta* **1989**, *157*, 143.

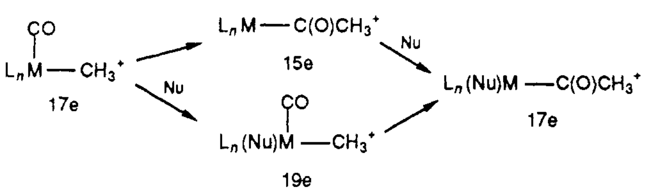
[5] (a) Magnuson, R. H.; Zulu, S.; T'sai, W.-M.; Giering, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6887. (b) Magnuson, R. H.; Meirowitz, R.; Zulu, S. J.; Giering, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 5790. (c) *Organometallics*, **1983**, 2, 460.

[6] (a) Doxsee, K. M.; Grubbs, R. H.; Anson, F. C. *J. Am. Chem. Soc.* **1984**, *106*, 7819. (b) Therien, M. J.; Trogler, W. C. *J. Am. Chem. Soc.* **1987**, *105*, 5127. (c) Reger, D. L.; Mintz, E.; Lebioda, L. *J. Am. Chem. Soc.* **1986**, *108* 1940.

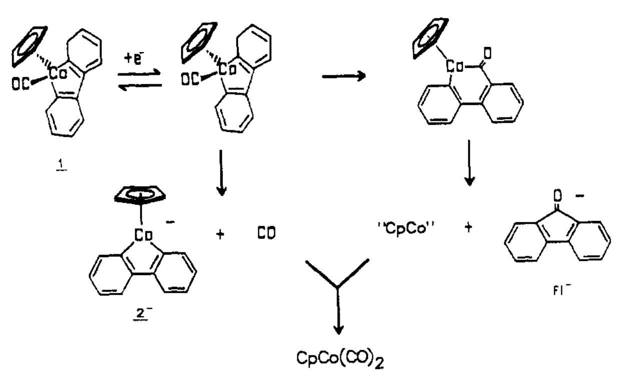
[7] Miholova, D.; Vlcek, A. A. *J. Organomet. Chem.* **1982**, *240*, 413.

[8] Wakatsuki, Y.; Nomura, O.; Tone, H.; Yamazaki, H. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1344.

Scheme I



Scheme II



that reduction of the phosphine-substituted analogues $Cp(PR_3)CoC_{12}H_8$ involved an orbital that is antibonding between Co and the phosphine ligand, quantitatively producing PR_3 and the 17e anion 2^-.[10,11] Although some 2^- is also formed upon reduction of 1 in thf, significant quantities of the insertion product fluorenone anion, Fl^-, are generated immediately after electron uptake. The replacement of Co by CO in the fluorenyl backbone must result from a remarkably fast carbonyl migratory insertion reaction[8,13] in which the 19e complex 1^- precedes the insertion step. A possible structure of the initial insertion product is shown in Scheme II. The 19e anion 1^- is very short-lived, and cyclic voltammetric (CV) scans of 1 up to 10^4 V/s did not show reversibility for the one-electron wave $1/1^-$. The other product of this reaction is $CpCo(CO)_2$. Confirmation of the product identities has been obtained from their properties as measured by CV, exhaustive electrolyses, and IR and NMR spectra. Fluorenone was confirmed as being in its anion form from rotating-ring–disk electrode measurements.

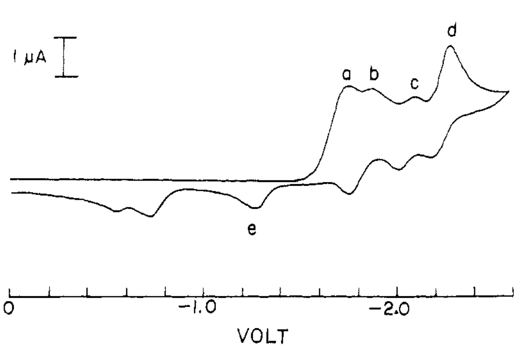


Figure 1. Cyclic voltammetric scan of 0.5 mM 1 in thf with v = 0.2 V/s at a Pt-bead electrode (potential vs SCE). The lettered waves arise from the following: reductions (a) 1, (b) $CpCo(CO)_2$, (c) fluorenone anion, Fl^-, and (d) 2^-; oxidation (e) fluorenone anion, Fl^-.

Consider the CV scans in Figure 1. Four cathodic peaks are seen at scan rates ranging from v = 0.05 to 100 V/s. Peaks a and d are due to the irreversible 1e reduction of 1 and the reversible reduction of 2^-, respectively. The other reversible waves are due to $CpCo(CO)_2^{0/-}$ (b, $E°$ = −0.82 V) and $Fl^{-/2-}$ (c, $E°$ = −2.02 V).[12] In addition to showing a reduction to the dianion, Fl^- is also responsible for peak e on the reverse scan, which is half of the reversible couple $Fl^{0/-}$ ($E°$ = −1.32 V). The anodic waves at yet more positive potentials (>−0.9 V) are due to the reoxidation of 2^-[11] and do not play a role in the insertion scheme. The assignments of all waves were confirmed by comparison with those of authentic samples.

Analyses of electrolyzed solutions by electrochemistry and by IR spectroscopy confirm the voltammetric results, with preliminary determinations of 0.3–0.4 equiv of $CpCo(CO)_2$, 0.25–0.50 equiv of Fl^-, and ca. 0.6 equiv of 2^- per equiv of 1, consistent with the approximate overall stoichiometry of the equation

$$3\,1 + 3e^- \rightarrow Fl^- + 2\,2^- + CpCo(CO)_2$$

This implies that the insertion reaction is competitive with the cleavage of the Co–CO bond, since the formation of $CpCo(CO)_2$ most likely occurs from the reaction of free CO with "CpCo" liberated in the insertion process. In this model, the metal limits the degree of conversion to fluorenone by scavenging CO. Consequently, reduction under a CO atmosphere increases the formation of the insertion product, with CV scans showing a large increase in waves c and e (Fl^-) and the absence of wave d (2^-).

One other report of a reductively induced CO insertion reaction has appeared, involving $Cp(CO)Fe(CO)(CH_3)$.[7] The experimental conditions of that study, namely an excess of PPh_3 and a slow, electrocatalytic conversion to $Cp(CO)(PPh_3)Fe(COCH_3)$, complicate the mechanistic considerations, but it is quite likely that the insertion step occurs at the 19-electron stage in that system also.

We believe it is reasonable to assign a 19-electron structure to the metal in the transient anion 1^-, for a much more stable anion would be expected if the extra electron were localized in the fluorenyl hydrocarbon backbone. Thus, the present results strongly suggest that CO insertion can be accelerated in a formal 19-electron complex. The relationship between this observation and the behavior of true (CO)M–alkyl complexes is yet to be established, but our results are consistent with the observation of 19-electron intermediates in the CO insertion chemistry of $[Cp(CO)Fe(PPh_3)(CH_3)]^+$. This appears to be the first example of redox-accelerated migratory insertion accomplished in the absence of an added nucleophile.[13] Since neutral 1 must be heated under CO to produce fluorenone[8] whereas 1^- gives the insertion product at room temperature in less than 10^{-2} s, it is clear that the 19e complex has an enormously enhanced rate of migratory insertion.

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(9) This statement assumes that the Cp ligand remains η^5-bonded to the metal in 1^-. As pointed out by Therien and Trogler,[6b] Cp slippage is often very hard to disprove, but it is much more likely to play a role in 20e/18e systems than in 19e/17e systems. Recent examples of symmetrically bonded C_5R_5 complexes of 19-electron metals are relevant. $(\eta^5\text{-}C_5Ph_5)Co(CO)_2^-$: Connelly, N. G.; Lane, G. A.; Raven, S. J.; Rieger, P. H.; Geiger, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 6219. $(\eta^6\text{-arene})Rh(\eta^5\text{-}C_5Me_5)^+$: Merkert, J.; Nielson, R. M.; Weaver, M. J.; Geiger, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 7084.

(10) Kelly, R. S.; Geiger, W. E. *Organometallics* **1987**, *6*, 1432.

(11) Donovan, B. T.; Geiger, W. E. *J. Am. Chem. Soc.* **1988**, *110*, 2335. As discussed in this reference and ref 10, the LUMO of $Cp(L)CoC_{12}H_8$ is predominantly located on the metal and is antibonding between Co and L, causing scission of the Co–L bond upon reduction.

(12) Kalinowski, M. K.; Grabowski, Z. R.; Pakula, B. *Trans. Faraday Soc.* **1966**, *62*, 918.

(13) Theoretical studies of the mechanism of migratory insertions are available: (a) Berke, H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7224. (b) Shusterman, A. J.; Tamir, I.; Pross, A. *J. Organomet. Chem.* **1988**, *340*, 203. (c) Axe, F. U.; Marynick, D. S. *J. Am. Chem. Soc.* **1988**, *110*, 3728.