tion was used.[37] The reference electrode was an SCE (Tacussel) separated from the solution by a bridge (3 mL) filled with a n-Bu_4NBF_4 solution in THF identical with that used in the cell. All potentials given here refer to this reference electrode. All the experiments reported here were performed at 20 °C.

Electron consumptions in transient electrochemistry were determined following a method previously described that combines the use of classical working electrodes and ultramicroelectrodes.[9] Other electrochemical procedures are identical with those previously described.[11] Carbon dioxide concentration was determined according to the procedure described in ref 3p.

Preparative Scale Reductions of (σ-Aryl)palladium(II) Complexes in the Presence of Carbon Dioxide. The divided cell, experimental setup, and procedures were identical with those previously described.[3p,11] Anhydrous carbon dioxide (Air Liquide) was continuously bubbled through the solution during the electrolysis so as to ensure constantly a saturating concentration. Electrolyses were performed with 0.5 mmol of starting material dissolved in 50 mL of THF, 0.3 M NBu_4BF_4 (catholyte). A lithium rod was used as a sacrificial anode (anolyte: 15–20 mL of THF, 0.3 M NBu_4BF_4). The electrolyses were interrupted when the current reached 5–6 mA (limit for background current). The catholyte was poured into 200 mL of sodium hydroxide solution (1 N in water). The mixture was extracted three times with 80 mL of Et_2O. The organic phase was dried over $MgSO_4$, filtered, and evaporated. Aromatic compounds were identified (Ar–Ar; no ArH derivative could be observed) and titrated using 250-MHz ^1H NMR, by dissolving the residue in 1 mL of $CDCl_3$ with 1,1,2,2-tetrachloroethane as an internal standard, and comparison with authentic samples. The aqueous phase was acidified to pH = 3–4 with HCl, 1 N. It was then extracted three times with 80 mL of Et_2O, dried over $MgSO_4$, filtered, and evaporated. The yield in $ArCO_2H$ was then determined using 250-MHz ^1H NMR, by dissolving the residue in 1 mL of $CDCl_3$ with 1,1,2,2-tetrachloroethane as an internal standard, and comparison with authentic samples of the carboxylic acids. For the case of the cyano derivative, p-terephthalic acid was isolated, owing to the facile hydrolysis of the cyano group under the basic conditions prevailing either during the electrolysis or during the workup of the solution.

Acknowledgment. This work has been supported in part by CNRS (URA 1110 Activation Moléculaire) and by ENS. Partial financial support from SNPE (Contract No. 14/89) and EDF (Contract No. OT-E53L31) is also acknowledged. Mr. Serge Negri is acknowledged for his kind technical assistance during some of the electrosynthetic experiments reported in Table I.

Registry No. $Pd^{II}Cl_2(PPh_3)_2$, 13965-03-2; $Pd^{II}Cl_2(PBu_3)_\infty$, 14977-08-3; $Pd^{II}Cl_2(dppe)$, 19978-61-1; $Pd^{II}Cl_2(dpp)$, 59831-02-6; $C_6H_5Pd^{II}Br(dppe)$, 142438-84-4; $C_6H_5Pd^{II}Br(PPh_3)_2$, 30643-33-5; $C_6H_5Pd^{II}Br(PPh_3)_2$, 30643-33-5; p-$CH_3C_6H_4Pd^{II}I(PPh_3)_\infty$, 142507-62-8; p-$CH_3COC_6H_4Pd^{II}Br(PPh_3)_2$, 37474-29-6; p-$CNC_6H_4Pd^{II}Br(PPh_3)_2$, 142507-61-7; $Pd^0(PPh_3)_4$, 14221-01-3; $C_6H_5Pd^{II}Cl(PPh_3)_2$, 63864-53-9; $C_6H_5Pd^{II}I(PPh_3)_2$, 55123-60-9; PPh_3, 603-35-0; p-CNC_6H_4Br, 623-00-7; $C_6H_5CO_2H$, 65-85-0; p-$CH_3C_6H_4CO_2H$, 99-94-5; p-$CH_3COC_6H_4CO_2H$, 586-89-0; p-$CO_2HC_6H_4CO_2H$, 100-21-0; CO_2, 124-38-9; C_6H_5OH, 108-95-2; C_6H_5Br, 108-86-1; p-$CH_3C_6H_4I$, 624-31-7; p-$CH_3COC_6H_4Br$, 99-90-1; (p-$CH_3COC_6H_4)_2$, 787-69-9; $C_6H_5Pd^{II}(dppe)$, 60674-49-9.

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One-Electron Oxidative Cleavage of Palladium(II) Alkyl and Phenoxo Bonds

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Abstract: One-electron oxidation of the d^8 dialkyls $Pd(CH_3)_2(dmpe)$, $Pd[CH_2Si(CH_3)_3]_2(dmpe)$, and $Pd(CH_3)[P(t\text{-}Bu)_2(CH_2)_2CH(CH_2)_2P(t\text{-}Bu)_2]$, where dmpe = 1,2-bis(dimethylphosphino)ethane, by chemical or electrochemical methods results in homolytic cleavage of the Pd–alkyl bond to produce an alkyl radical and the corresponding cationic palladium(II) monoalkyl complex. In the presence of a trapping ligand, PPh_3, oxidation of $Pd[CH_2Si(CH_3)_3]_2(dmpe)$ with $[FeCp_2]PF_6$, Cp = η-C_5H_5, produces $Si(CH_3)_4$ and $[CH_2Si(CH_3)_3]_2$ in a ratio similar to that obtained from the reaction between $MgCl[CH_2Si(CH_3)_3]$ and $[FeCp_2]PF_6$. Because of the chemical irreversibility of the homolytic cleavage process, uphill electron transfer between $Pd[CH_2Si(CH_3)_3]_2(dmpe)$ and electrochemically generated $FeCp_2^{\bullet+}$ could be observed with $k = 46 \pm 7\ M^{-1}\ s^{-1}$ at 60 °C. The oxidative cleavage reactions also exhibit selectivity. Oxidation of $Pd(CH_3)[P(t\text{-}Bu)_2(CH_2)_2CH(CH_2)_2P(t\text{-}Bu)_2]$ results in exclusive loss of the CH_3 group, and oxidation of $Pd(CH_3)(OPh)(dmpe)$ results in preferential cleavage of the Pd–O bond. These results suggest the oxidative cleavage chemistry developed for d^0 metal alkyls can be extended to late transition metals.

Introduction

Coordinatively unsaturated metal species act as highly reactive intermediates in hydrogenation, hydrosilylation, hydroformylation, and other reactions catalyzed by soluble transition metal complexes.[1] Mechanistic studies show that these complexes usually result from ligand dissociation or reductive elimination processes. Coordinative unsaturation has also been generated by photolysis, thermolysis, and electron transfer and with acidic, basic, or radical initiators.[2] Under the proper conditions stable complexes can be isolated.[2,3] Jordan et al. have reported that the reaction between Cp_2ZrR_2 and $[Ag][BPh_4]$[4] or $[Cp_2Fe][BPh_4]$[5] yields the $[Cp_2ZrR]^+$ cation, which is an active ethylene polymerization catalyst. These highly reactive intermediate species are useful catalysts and often exhibit unique reactivity.[2,3]

Previous research in our laboratory has explored the generation and subsequent reactivity of "$Pt(PR_3)_2$" and "$Pd(PR_3)_2$" coor-

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dinatively unsaturated metal species.[6] More recently we have reported the synthesis of palladium(II)–amine complexes by protonolysis reactions of palladium–alkyls by ammonium salts.[7] These reactions initially generate a 14-electron three-coordinate "$[Pd(dmpe)Me]^{+}$" cationic intermediate, which is trapped in the presence of amine. Here we describe an alternative method for the generation of these species: the chemical and electrochemical one-electron oxidative cleavage of palladium–alkyl and –phenoxo bonds. This suggests that the one-electron oxidative cleavage reactions discovered for d^0 silyls[3f] and alkyls[4,5] may be generalized to electron-rich late transition metal systems.

Experimental Section

Materials. All reactions were performed under a nitrogen atmosphere by using modified Schlenk and glovebox techniques. Liquids were transferred by syringe (or cannula). Materials obtained from commercial sources were used without further purification, except where noted. Under a nitrogen atmosphere, Et_2O and *n*-pentane were dried over sodium benzophenone ketyl. Methylene chloride and acetonitrile were distilled over CaH_2. The compounds $PdMe_2(dmpe)$ (**1**),[8] $Pd(CH_2SiMe_3)_2(dmpe)$ (**2**),[8] PdMe(OPh)(dmpe) (**3**),[9,10] and bis(di-*tert*-butylphosphino)pentan-3-yl-CPP′]methylpalladium(II)[11] (**5**) were prepared according to known procedures. The sample of $Me_3SiCH_2CH_2SiMe_3$ was produced independently by a Grignard coupling reaction with $NiCl_2(dppe)$ as catalyst.

Spectral Data. All NMR spectra were recorded on a GE QE-300 MHz NMR spectrometer equipped with a 5-mm broad band probe. ^1H NMR chemical shifts were referenced to the residual solvent peak in the observed spectra. All $^{31}P\{^1H\}$ NMR spectra were referenced to the deuterated lock solvent, which had been previously referenced to 85% H_3PO_4, with downfield shifts being positive. IR spectra were recorded on a Mattson Instruments Galaxy 2020 FT-IR spectrometer.

Electrochemical Studies. Both cyclic voltammetry and controlled-potential bulk electrolysis measurements were carried out under an inert atmosphere with a BAS-100 electrochemical analyzer. A J-shaped platinum working electrode with about a 0.2 mm² surface area, a platinum wire auxiliary electrode, and a silver wire reference electrode were employed for the cyclic voltammetry experiments. A platinum gauze of high surface area, a platinum wire auxiliary electrode, and a silver wire reference electrode were employed in a three-compartment cell separated by fritted glass disks for bulk electrolysis. No IR compensation was used in the double potential step measurements, and the analysis of Q vs $t^{1/2}$ plots showed that capacitative charging effects did not alter the charge ratios appreciably (<5%) over the range of pulse widths used in the kinetic analysis. The CV and bulk electrolysis experiments were performed in CH_2Cl_2 or CH_3CN solvent at room temperature, 0.1 M in supporting electrolyte (tetra-*n*-butylammonium hexafluorophosphate or tetra-*n*-butylammonium tetrafluoroborate) and 1.0 mM in palladium complex.

***cis*-(Bis(dimethylphosphino)ethane)((trimethylsilyl)methyl)phenoxopalladium(II), $Pd(CH_2SiMe_3)(OPh)(dmpe)$, 4.** To $Pd(CH_2SiMe_3)_2(dmpe)$ (**2**) (0.300 g, 0.70 mmol) was added a solution of phenol (0.065 g, 0.70 mmol) in C_6H_6 (10 mL). The colorless solution was stirred for 16 h giving a colorless precipitate. The solvent concentration was reduced under vacuum to ~3 mL and the remaining solution was filtered. The solid residue was dissolved in CH_2Cl_2 and stirred with activated charcoal for 15 min. This was filtered, yielding a pale yellow solution, and the volume was reduced to 1.5 mL. This solution was layered with Et_2O (15 mL) to yield colorless crystals of **4**, 0.231 g (72%): mp 147–150 °C dec. ^1H NMR (CD_3CN) δ 0.02 (s, 9 H, $SiCH_3$), 0.14 (dd, $^3J_{PH(trans)} = 12$ Hz, $^3J_{PH(cis)} = 5$ Hz, 2 H, $PdCH_2$) 1.13 (d, $^2J_{PH} = 9$ Hz, 6 H, PCH_3), 1.54 (d, $^2J_{PH} = 6$ Hz, 6 H, PCH_3), 6.24 (t, 1 H, OC_6H_5), 6.52 (d, 2 H, OC_6H_5), 6.89 (d, 2 H, OC_6H_5). $^{31}P\{^1H\}$ NMR (CD_3CN) δ 27.37 (s, $^2J_{PP} = 18$ Hz) 40.22 (s, $^2J_{PP} = 18$ Hz). Anal. Calcd for $C_{16}H_{32}OP_2PdSi$: C, 43.99; H, 7.38. Found C, 43.98; H, 7.33.

(Acetonitrile)(bis(dimethylphosphino)ethane)((trimethylsilyl)methyl)palladium(II) Tetraphenylborate, $[Pd(CH_2SiMe_3)(dmpe)(CH_3CN)][BPh_4]$, 6. With the exclusion of light, a suspension of $AgBPh_4$ (0.185 g, 0.43 mmol) in CH_3CN (5 mL) was added to a solution of $Pd(CH_2SiMe_3)_2(dmpe)$ in CH_3CN (5 mL). The solution was stirred for 20 min at which time a black precipitate had formed. The solution was filtered and the pale yellow filtrate was concentrated to 3 mL, layered with Et_2O (15 mL), and put in the freezer to yield white flakes of **6**, 0.052 g (17%): mp 162–164 °C dec. ^1H NMR (CD_3CN) δ 0.04 (s, 9 H, $SiCH_3$), 0.26 (dd, $^3J_{PH(trans)} = 12$ Hz, $^3J_{PH(cis)} = 4$ Hz, 2 H, $PdCH_2$), 1.47 (d, $^2J_{PH} = 10$ Hz, 6 H, PCH_3), 1.57 (d, $^2J_{PH} = 11$ Hz, 6 H, PCH_3), 2.14 (s, 15 H, CH_3CN), 6.83 (t, 4 H, BC_6H_5), 6.96 (t, 8 H, BC_6H_5), 7.26 (m, 8 H, BC_6H_5). $^{31}P\{^1H\}$ NMR (CD_3CN) δ 45.97 (d, $^2J_{PP} = 23$ Hz), 33.08 (d, $^2J_{PP} = 23$ Hz). IR (KBr, cm^{-1}) 2203, 2219 (CN). Solutions of **6** decompose slowly so the isolated solid is usually ~20% contaminated with a species that exhibits a ^{31}P resonance at δ 34.2. The solution of **6** generated initially is, however, free of this impurity.

Reaction of 1, 2, and 5 with $[Cp_2Fe][PF_6]$ in CD_3CN. Complexes **1**, **2**, or **5** (0.010 g) and $[Cp_2Fe][PF_6]$ (1 equiv) were loaded into an NMR tube and CD_3CN (0.45 mL) was added. The initial purple color of the ferrocinium cation rapidly disappears to yield a yellow-orange solution. The ^1H and $^{31}P\{^1H\}$ NMR spectra of $[Pd(dmpe)(CH_2SiMe_3)(CH_3CN)][PF_6]$ resulting from **2** are similar to that of **6**. Spectral data for $[Pd(dmpe)Me(CD_3CN)][PF_6]$ resulting from the reaction of complex **1**: ^1H NMR (CD_3CN) δ 0.28 (dd, $^3J_{PH(trans)} = 7$ Hz, 2 H, $PdCH_3$), 1.50 (d, $^2J_{PH} = 9$ Hz, 6 H, PCH_3), 1.59 (d, $^2J_{PH} = 12$ Hz, 6 H, PCH_3), 6.83 (t, 4 H, BC_6H_5). $^{31}P\{^1H\}$ NMR (CD_3CN) δ 26.67 (d, $^2J_{PP} = 24$ Hz), 41.41 (d, $^2J_{PP} = 24$ Hz). Spectral data of (acetonitrile)[1,5-bis(di-*tert*-butylphosphino)pentan-3-yl-CPP′]palladium(II) hexafluorophosphate resulting from the reaction with complex **5**: ^1H NMR (CD_3CN) 1.48 (q, 36 H, CCH_3), 3.22 (m br, 1 H, $PdCH$). $^{31}P\{^1H\}$ NMR (CD_3CN) δ 94.24 (s).

Organic Products from the Reaction between 2, $[Cp_2Fe][PF_6]$, and Triphenylphosphine. Complex **2** (0.157 g, 0.36 mmol), $[Cp_2Fe][PF_6]$ (0.121 g, 0.36 mmol), and PPh_3 (0.095 g, 0.36 mmol) were combined in one bulb of a vacuum transfer apparatus and CH_2Cl_2 (1 mL) was added. The solution turned yellow-orange and was stirred for 1 h. At this time all the volatiles were vacuum transferred and the resulting solution was analyzed. ^1H NMR (C_6D_6) δ −0.09 (s), 0.01 (s), 0.41 (s). These products were shown to be TMS (~57%) and $Me_3SiCH_2CH_2SiMe_3$ (~43%) by comparison with authentic samples. The ^1H and $^{31}P\{^1H\}$ NMR spectra of the remaining solid residue showed the formation of $Pd(CH_2SiMe_3)(dmpe)(PPh_3)^{+}$. ^1H NMR (C_6D_6) δ −0.26 (s, 9 H, $SiCH_3$), 0.02 (s), 0.41 (s), 0.68 (d, $^2J_{PH} = 7$ Hz, 6 H, PCH_3), 1.55 (d, $^2J_{PH} = 7$ Hz, 6 H, PCH_3), 2.0 (m, 4 H, PCH_2), 4.00 (s), 4.27 (s), 7.05 (m, C_6H_5), 7.35 (m, C_6H_5). $^{31}P\{^1H\}$ NMR (C_6D_6) δ 22.89 (dd, $^2J_{PP(cis)} = 39$ Hz), 25.18 (dd, $^2J_{PP(cis)} = 39$ Hz, $^2J_{PP(trans)} = 408$ Hz), 37.95 (dd, $^2J_{PP(cis)} = 39$ Hz, $^2J_{PP(trans)} = 408$ Hz). A similar reaction performed in the absence of triphenylphosphine resulted in complete decomposition of the metal complex, and the volatiles yielded almost exclusively the alkyl coupling product $Me_3SiCH_2CH_2SiMe_3$.

Reaction between Me_3SiCH_2MgCl and $[Cp_2Fe][PF_6]$. $[Cp_2Fe][PF_6]$ (0.014 g, 0.04 mmol) was loaded into a NMR tube. To this was added CD_2Cl_2 (0.45 mL) and Me_3SiCH_2MgCl (0.04 mL, 1.0 M in Et_2O). The initial dark purple color of ferrocinium was immediately replaced by the orange color of ferrocene. An initial ^1H NMR spectrum was taken but was very broad. Addition of small quantities of methanol killed a very slight excess of Grignard and resulted in a sharper spectra for the TMS (~50%) and $Me_3SiCH_2CH_2SiMe_3$ (~50%).

Reaction of 4 and $[Cp_2Fe][PF_6]$ in CD_3CN. Complex **4** (0.010 g, 0.02 mmol) and $[Cp_2Fe][PF_6]$ (0.011 g, 0.03 mmol) were combined in an NMR tube and CD_3CN (0.45 mL) was added to give a yellow-orange solution with excess $[Cp_2Fe][PF_6]$ precipitate present. The ^1H and $^{31}P\{^1H\}$ NMR spectra of this solution were similar to **6**, except for additional resonances in the ^1H NMR spectrum from the aryl protons. ^1H NMR (CD_3CN) δ 6.78 (m, 3 H, OC_6H_5) and 7.19 (t, 2 H, OC_6H_5).

Reaction of 6 and Sodium Phenoxide. Complex **6** (0.010 g, 0.01 mmol) and NaOPh (0.008 g, 0.07 mmol) were combined in a NMR tube with CD_3CN (0.45 mL). At 25 °C only resonances resulting from **4** were observed. Heating the solution to 60 °C for 0.5 h resulted in the appearance of two new resonances in the $^{31}P\{^1H\}$ NMR spectrum. $^{31}P\{^1H\}$ NMR (CD_3CN) δ 27.53 (d, $^2J_{PP} = 16$ Hz), 33.33 (d, $^2J_{PP} = 16$ Hz).

Results and Discussion

One-Electron Oxidative Cleavage of Palladium–Alkyls. The reaction between $Pd(CH_2SiMe_3)_2(dmpe)$ (**2**) and $AgBPh_4$ in

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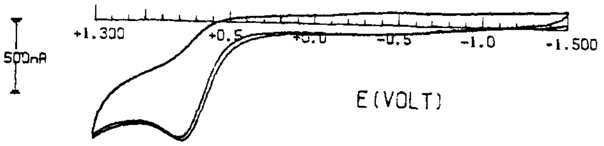


Figure 1. Cyclic voltammogram of 1.0 mM **2** in CH_3CN with 0.1 M $[NBu_4]PF_6$ vs an Ag wire pseudoreference at 200 mV/s.

Table I. Cyclic Voltammetric Oxidation Peak Potentials for Complexes **1–5**

complexes	E_p^a (V)^a
$PdMe_2(dmpe)$ (**1**)	0.60
$Pd(CH_2SiMe_3)_2(dmpe)$ (**2**)	0.75
$PdMe(OPh)(dmpe)$ (**3**)	0.61
$Pd(CH_2SiMe_3)(OPh)(dmpe)$ (**4**)	0.59
$PdMe[(t\text{-}Bu)_2P(CH_2)_2CH(CH_2)_2P(t\text{-}Bu)_2]$ (**5**)	0.51
NaOPh	0.16

^{a}Experimental conditions: [metal complex] = 1.0×10^{-3} M; [supporting electrolyte] = 0.1 M tetrabutylammonium hexafluorophosphate; temperature = 23 ± 2 °C, scan rate = 200 mV/s; platinum working electrode, platinum wire auxiliary electrode, and a silver wire reference electrode were used for the measurements. Potentials were referenced to a ferrocene internal standard with $E_{1/2} = 0.52$ V. Acetonitrile was used as the solvent for compounds **1**, **2**, and **5**, and CH_2Cl_2 was used for **3**, **4**, and NaOPh.

CH_3CN yields $[Pd(CH_2SiMe_3)(dmpe)(CH_3CN)][BPh_4]\cdot XCH_3CN$ (**6**). The palladium complex **6** was characterized by

$$Pd(CH_2SiMe_3)_2(dmpe) + AgBPh_4 \xrightarrow{CH_3CN} [Pd(CH_2SiMe_3)(dmpe)(CH_3CN)]^+ + Ag^0 \quad (1)$$

^1H and $^{31}P\{^1H\}$ NMR and IR spectroscopies. The low isolated yield was a result of its instability in solution, because quantitative conversion to **6** was observed by NMR spectroscopy. In the solid state under a N_2 atmosphere complex **6** appears stable at room temperature indefinitely. Solutions slowly decompose over several days in CD_3CN solvent, while CD_2Cl_2 solutions decompose more rapidly over 0.5 h.

Similar oxidative cleavage reactions have been reported for Cp_2ZrMe_2[5] and *fac*-$IrMe_3(PMe_2Ph)_3$.[12] Two mechanisms of metal–alkyl bond cleavage have been proposed. The reaction between Cp_2ZrMe_2 and $AgBPh_4$ to yield $[Cp_2ZrMe]^+$ and ethane was originally hypothesized to proceed through methyl abstraction by Ag^+. A similar pathway was assumed for the reaction of *fac*-$IrMe_3(PMe_2Ph)_3$ with $[Cu(CH_3CN)_4][BF_4]$. Later, Jordan et al. reported that the reaction between $Cp_2Zr(CH_2Ph)_2$ and $[Cp_2Fe][BPh_4]$ yields $[Cp_2ZrCH_2Ph]^+$, ferrocene, and $PhCH_2CH_2Ph$.[6] This reaction was proposed to proceed by a one-electron oxidative cleavage pathway. Subsequent electrochemical studies of the oxidation reactions of Cp_2TiR_2 and Cp_2ZrR_2 systems further support these conclusions and establish an outer-sphere mechanism for electron transfer.[13]

Electrochemical experiments may help distinguish a one-electron oxidative cleavage pathway from a methyl abstraction reaction. Complex **2** generates an irreversible oxidation wave in CH_3CN and CH_2Cl_2, as shown in Figure 1. Bulk electrolysis of **2** in CH_2Cl_2 establishes this reaction to be a clean one-electron process. $[Cp_2Fe][PF_6]$ also proved to be an effective oxidant for complex **2**, to yield the hexafluorophosphate analogue of **6**. Reactions of other palladium–alkyl complexes with $[Cp_2Fe][PF_6]$ yielded similar results. The palladium–methyl bond of **1** was cleaved rapidly and resulted in the formation of the corresponding cationic acetonitrile complex. Cyclic voltammetry confirmed that this reaction was also an irreversible one-electron oxidation process.

Ferrocene was added to the cyclic voltammetry solution as a reference to quantify the oxidation potential of the palladium-alkyls (Table I); however, the standard reversible one-electron wave of ferrocene displayed a reduction wave of diminished intensity. A series of cyclic voltammetry experiments were conducted to determine the concentration dependence of these results. Increasing the concentration of **1** from 0.0 mM stepwise to 10.0 mM, while holding the concentration of ferrocene constant, resulted in the disappearance of the reduction wave of ferrocene as more of **1** is added (Figure 2). One explanation of this phenomenon is that the electrochemically produced ferrocinium reacts with complex **1** in a chemical step, before it is reduced back

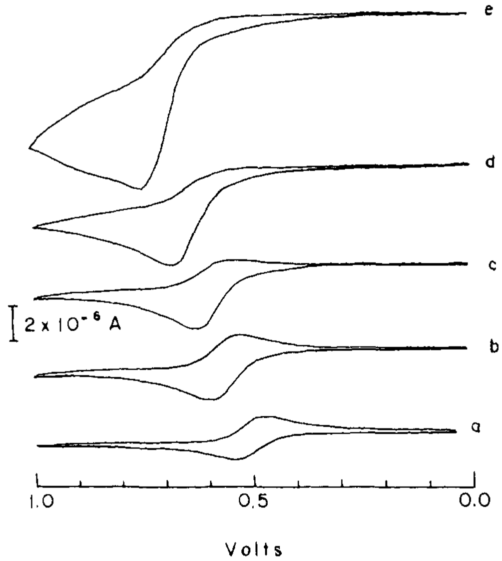


Figure 2. Cyclic voltammograms of $FeCp^*_2$ (1.0 mM) and tetrabutylammonium tetrafluoroborate (0.1 M) with varying concentrations of **1** (*a* = 0.0 mM, *b* = 1.0 mM, *c* = 2.0 mM, *d* = 5.0 mM, *e* = 10.0 mM) in CH_3CN at a constant scan rate of 200 mV/s at room temperature.

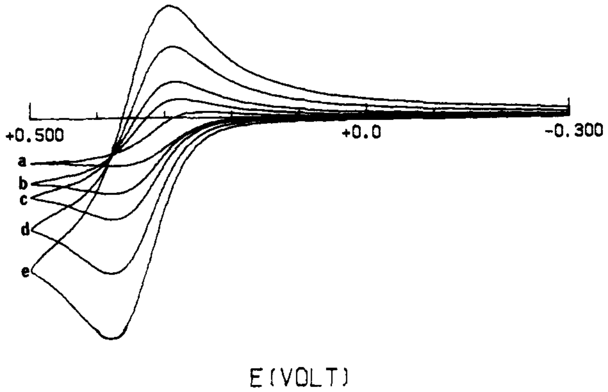
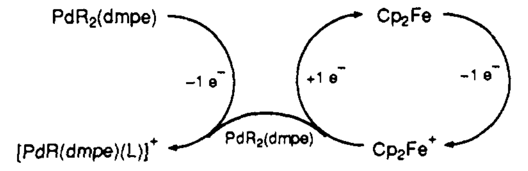


Figure 3. Cyclic voltammograms of $FeCp^*_2$ (1.0 mM) vs an Ag wire pseudoreference with 25.0 mM $Pd(CH_2SiMe_3)_2(dmpe)$ present at 60 °C. The electrolyte is 0.1 M $[NBu_4]BF_4$ in CH_3CN and the scan rate varies: (a) 50, (b) 100, (c) 200, (d) 500, and (e) 1000 mV/s.

Scheme I. The Electrochemical Generation of **6** in the Presence of Ferrocene



Scheme II

$$\text{E} \qquad FeCp_2^* \rightleftharpoons FeCp_2^{*+} + e$$

$$\text{C} \qquad FeCp_2^{*+} + PdR_2(dmpe) \xrightarrow{k} FeCp_2^* + PdR(dmpe)(NCCH_3)^+ + {}^\bullet R$$

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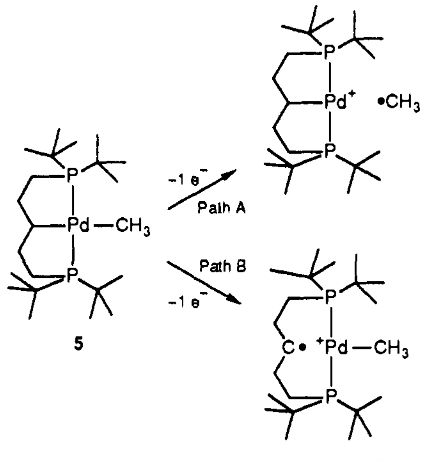
Scheme III. Two Possible One-Electron Oxidative Cleavage Pathways for the Different Palladium–Alkyl Bonds in Complex **5**



to ferrocene at the electrode surface, as shown in Scheme I. This reaction scheme has been discussed by Saveant et al.[14] for organic systems. When the electron transfer reaction between the two soluble redox components is irreversible, because of a following chemical reaction (homolysis of the Pd–CH_3 bond in the present case), then even uphill electron transfer reactions can be observed.

Figure 3 shows the couple for decamethylferrocene ($FeCp^*_2/E_{1/2} = 0.05$ V) when $Pd(CH_2SiMe_3)_2$(dmpe) is also present in solution. At slow scan rates, 50 mV/s, the wave shape is that expected for a nearly irreversible oxidation process. This can be attributed to an EC second-order regeneration process, shown in Scheme II. The rate constant k was determined by double potential step chronocoulometry with the working curves in the literature,[15] and found to be $46 \pm 7\ M^{-1}\ s^{-1}$ at 60 °C. This electron transfer process is endoergic and therefore relatively slow.

The one-electron oxidation of the *trans*-palladium–dialkyl complex **5** creates the option for oxidation of two different palladium–alkyl bonds in one molecule. Cleavage of either the palladium–methyl bond or the chelated palladium–methylene bond is possible. The two pathways are shown in Scheme III. Cyclic voltammograms of **5** display an irreversible one-electron oxidation wave similar to that for **1** and **2**. The reaction of **5** with $[FeCp_2][PF_6]$ gives ^1H and $^{31}P\{^1H\}$ NMR spectra consistent with the selective cleavage of the palladium–methyl bond. This evidence suggests that the irreversible one-electron oxidation wave results only from palladium–methyl bond cleavage (path A in Scheme III). These results were intriguing, because the methyl radical is eliminated instead of the secondary alkyl radical. This is the opposite of the known stabilities of alkyl-substituted radicals.[16] In studies of oxidative cleavage of Cp_2ZrRR' complexes with one-electron oxidants and proton donors, a significant steric effect on reactivity was observed.[17] Steric considerations may help explain the reactivity of **5**.

Cleavage of the chelated palladium–methylene bond in **5** (path B in Scheme III), which is not observed in the final products, may occur simultaneously. If this process is reversible and fast then the overall reaction would only display palladium–methyl bond cleavage, since this process is irreversible. Alternatively, if this reaction is slower than the irreversible oxidative cleavage of the palladium–methyl bond, it will also not be observed. The solid-state structure of **5** suggests a different explanation. The palladium–methyl bond in **5** is approximately 0.03 Å longer than the chelated palladium–methylene bond.[11] If this bond length difference reflects bond strength, and not simply a steric phenomenon, then this would explain the selective cleavage observed. In support of this explanation, protonolysis of **5** by weak acids also causes preferential cleavage of the palladium–methyl bond.[11]

Identification of the Organic Products from the One-Electron Oxidative Cleavage of Palladium–Alkyls. Jordan et al. reported that the organic product produced by the reaction between Cp_2ZrMe_2 and $AgBPh_4$ was ethane.[4] Similarly $Cp_2Zr(CH_2Ph)_2$ and $[FeCp_2][BPh_4]$ led to the radical coupling product $PhCH_2CH_2Ph$ and traces of benzylferrocene.[5] The reactions of **1**, **2**, and **5** with $AgBPh_4$ or $[Cp_2Fe][PF_6]$ also yield what appears to be alkyl–radical coupling products. Ethane was observed in the reaction solution of **1** and $[FeCp_2][PF_6]$ by ^1H NMR spectroscopy. The reaction between **2** and $[FeCp_2][PF_6]$ in the presence of PPh_3 yielded a solution containing $[Pd(CH_2SiMe_3)(dmpe)(PPh_3)][PF_6]$, ferrocene, and small amounts of another ferrocene derivative. No direct binding of PPh_3 to **2** was detected by ^{31}P NMR measurements. Analysis of the volatile products from this reaction revealed TMS (~57%) and $Me_3SiCH_2CH_2SiMe_3$ (~43%). These compounds were identified by their comparison to authentic samples in the ^1H NMR spectrum. The new ferrocene byproduct observed at δ 4.27 could possibly result from the coupling of the (trimethylsilyl)methyl radical and ferricinium, as has been observed with phenyl radicals.[18] These results are consistent with a one-electron oxidative cleavage mechanism, since the products appear to be derived from radical species. The oxidation of Me_3SiCH_2MgCl with $[FeCp_2][PF_6]$ yields roughly the same product ratio (50:50) of TMS to $Me_3SiCH_2CH_2SiMe_3$. This reaction should generate the $^{\bullet}CH_2SiMe_3$ radical.

When **2** is oxidized with $[FeCp_2][PF_6]$ in the absence of triphenylphosphine, the radical coupling product $Me_3SiCH_2CH_2SiMe_3$ forms as the dominant volatile organic product (in excess of 90%). It appears that the $^{\bullet}CH_2SiMe_3$ radical, produced by one-electron oxidation, attacks the remaining palladium–alkyl bond. The alkyl radical may form an initial radical pair $[Me_3SiCH_2{}^{\bullet}][Pd(dmpe)CH_2SiMe_3]^+$. If no ligand is present to trap the highly reactive cation, the labile coordination site may be attacked by the alkyl radical to produce the coupling product. These observations may be relevant to the use of PdL_2 systems as alkyl coupling catalysts. It suggests that oxidatively induced "reductive elimination" need not be a concerted process when d^8 systems are oxidized.

Reactivity of the [PdR(L_2)] Cation. Coordinatively unsaturated cationic complexes $[PdRL_2]^+$, generated by one-electron oxidation of the dialkyl complexes, can be trapped by two electron donating ligands. Phosphines, phosphites, arsines, amines, and nitriles have all been shown to form stable complexes with these cations.[7] Stabilization of the coordinatively unsaturated cationic complexes by a poor ligand, such as acetonitrile, has proved to be a synthetically useful form of these species. Addition of an anionic phenoxide ligand to **6** forms the stable palladium complex **4** by the nucleophilic attack of phenoxide on the metal center.

$$\underset{\mathbf{6}}{[Pd(CH_2SiMe_3)(dmpe)(CH_3CN)][BPh_4]} + NaOPh \rightarrow \underset{\mathbf{4}}{Pd(CH_2SiMe_3)(dmpe)(OPh)} + NaBPh_4 \quad (2)$$

One-Electron Oxidative Cleavage of a Palladium–Phenoxide Bond. The bond strength differences of transition metal carbon, oxygen, and nitrogen bonds have received attention in the recent literature.[19] Direct comparison of the homolytic reactivity between two of these moieties contained in the same molecule provides a direct test of the relative bonding characteristics. The reaction between $[Cp_2Fe][PF_6]$ and PdR(OPh)(dmpe) {R = CH_3 (**3**), CH_2SiMe_3 (**4**)} in acetonitrile yields the same cationic complexes $[PdMe(dmpe)(CH_3CN)][PF_6]$ and **6**-PF_6, as discussed above. Thus, oxidation of the metal complexes selectively cleaves the palladium–oxygen bond. Cyclic voltammetry experiments con-

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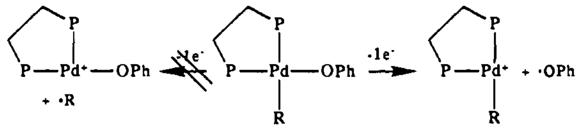
firmed these to be irreversible one-electron oxidation processes similar to the palladium–dialkyls. These potentials are given in Table I. The results qualitatively confirm the relative bond strength predictions for late metal–oxygen and late metal–carbon bonds.[19] It also shows that oxidative homolysis is not necessarily restricted to metal–alkyl bonds.



(3)

Conclusions

The reductive elimination of alkanes from palladium–dialkyl complexes is a well-established reaction pathway.[20] These reactions are usually achieved thermally and are believed to proceed by a mechanism involving ligand dissociation. Furthermore, palladium bis(phosphine) complexes are commonly used as catalysts for coupling two alkyl groups.[2] Oxidative processes were also known to induced reductive elimination of R–R, as has been reported for $[(bpy)_2Fe^{IV}R_2]^{2+}$ formed by the oxidation of $[(bpy)_2Fe^{III}R_2]^{+}$.[21] Therefore, the one-electron oxidative cleavage of palladium–alkyl bonds was an unforseen result.

Oxidative cleavage of zirconium–alkyl bonds is more easily rationalized. Zirconium(IV) has no d electrons, and only the bonding electrons of the ligands are available to be removed by oxidation. In PdR_2L_2 systems there are eight accessible nonbonding d electrons. Though related palladium(IV) compounds are known,[22] none were observed in these experiments. In all cases examined, the one-electron oxidation of palladium(II)–dialkyls and alkylphenoxides results in retention of the d^8 configuration of palladium(II). As in the zirconium(IV) case, only the predominantly bonding electrons of the ligands are involved in the net oxidation reactions. This contrasts with results obtained by Kochi et al. for the iron–alkyl systems where all the oxidations were reported to be metal based.[21] It is worth noting that the zirconium and palladium complexes are both even spin state systems (d^0, d^8 square planar), which exhibit similar oxidation chemistry and expulsion of an alkyl radical from an odd-electron intermediate. The $[(bpy)_2Fe^{III}R_2]^{+}$ intermediate complex, which chemically decomposes to yield an alkyl radical species,[21] is also of odd spin state (d^5 high spin). Only the even-electron $[(bpy)_2Fe^{IV}R_2]^{2+}$, produced by oxidation, undergoes reductive elimination to R–R. Whether this correlation with net spin is a general trend merits further study. A caveat is the possibility of efficient R–R coupling by attack of $R^\bullet$ on the M–R bond of a labile complex, as appears possible in the palladium systems when no trapping ligand is present.

The oxidation of zirconium- and palladium–alkyl complexes yields highly reactive metal complexes. The $[Cp_2ZrR]^+$ species has proven to be an effective ethylene polymerization catalyst.[4,5] The reactivity of $[(L_2)PdR]^+$ has not yet been fully explored. Several transition metal nitrile complexes are active nitrile hydration catalysts.[23] Late metal alkoxides and aryloxides have also been proposed as models for olefin hydration.[9] Carbon monoxide insertion into metal–carbon and other heteroatom bonds is another reaction proposed frequently in catalytic reactions.[1,2] Studies of the reactivity types discussed above are currently underway with these $[(L_2)PdR]^+$ reactive species.

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Direct Determination of Equilibrium Deuterium Isotope Effects at Natural Abundance

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Contribution from the Laboratoire de RMN et Réactivité Chimique, URA-CNRS 472 Université de Nantes, 2 rue de la Houssinière, 44072 Nantes Cedex, France. *Received March 5, 1991. Revised Manuscript Received January 10, 1992*

Abstract: A great variety of techniques has been used to study deuterium–protium partitioning in exchanging systems at equilibrium. In this context it is shown that the determination of site-specific isotope contents by ^{2}H-NMR at natural abundance provides simple and direct access to thermodynamic isotope fractionation factors. This method avoids the recourse to deuterated species and therefore the approximations inherent in the analysis of complex isotopomeric mixtures. A number of slowly exchanging systems involving OH, NH, or SH groups and water offer suitable conditions (large chemical shift differences, moderate line widths, ...) for the relatively accurate determination of thermodynamic fractionation factors. Moreover multiple fractionations can be observed and compared in ternary mixtures.

Knowledge of the thermodynanic fractionation factors in exchanging systems at equilibrium is of considerable interest for interpreting chemical or biochemical mechanisms. In this respect, hydrogen isotope exchange processes between water and exchangeable groups (OH, NH, SH, ...) occur frequently in biological media. A great deal of effort has been devoted to the determination of the equilibrium partitioning of deuterium and protium using a wide variety of experimental[1-13] and theoretical[14] methods. The experimental determinations require the use of

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