

Photochemistry of dipalladium(I) hexakis(methyl isocyanide) hexafluorophosphate

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Organometallics, **1983**, 2 (6), 767-769 • DOI: 10.1021/om00078a014 • Publication Date (Web): 01 May 2002

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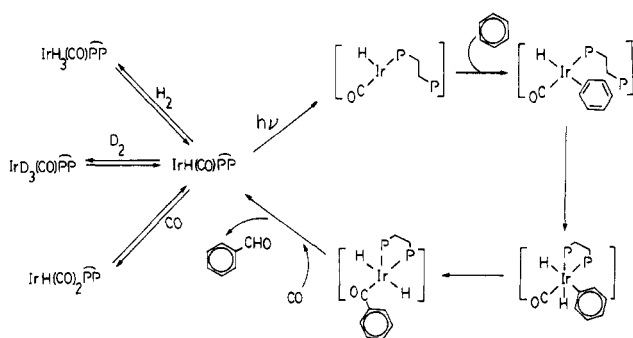
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Scheme I



nificant is benzyl alcohol,¹⁶ since the reduction of benzaldehyde to benzyl alcohol is thermodynamically favorable. This reaction may thus serve as a drain for the carbonylation of benzene to benzaldehyde and efforts in this direction are in progress.

The mechanism by which benzene C-H activation occurs is clearly photochemical and is not simply analogous to H₂ oxidative addition. One possibility is that the intermediate species IrH(CO)(dppe), which forms readily under either photolysis or thermolysis conditions, undergoes a photochemical dissociation of a ligand to form a 14-electron species facilitating arene coordination prior to oxidative addition. Alternatively, we may be witnessing an example of a photochemical oxidative addition reaction. Once the benzene C-H bond is activated, the carbonylation reaction probably follows the expected path of insertion and reductive elimination. We summarize the observed reaction chemistry and these mechanistic proposals in Scheme I.

Acknowledgment. We wish to thank the National Science Foundation (Grant CHE80-11974) and the Office of Naval Research for support of this work, as well as the Sherman Clarke Foundation for a fellowship to B.J.F. We also thank the Johnson Matthey Co., for a generous loan of precious metal salts and acknowledge Professor William Jones, Professor Jack Kampmeier, Dr. Curt Johnson, and Mr. Frank Feher for helpful discussions.

Registry No. 1, 85421-67-6; 2, 85421-68-7; 3, 85421-69-8; 4, 85421-70-1; 5, 85421-71-2; 6, 85421-72-3; dppe, 1663-45-2; [Bu₄N][Ir(CO)₂I₂], 60255-19-8; C₆H₆, 71-43-2; benzaldehyde, 100-52-7.

(16) Benzyl alcohol was detected and quantified by GLC (FID) on a combination column consisting of 10 ft of Apiezon L on Chromosorb W and 10 ft of 20% SE-30 on Chromosorb W using the same GLC conditions as in ref 11. Its formation was confirmed by coinjection with an authentic sample of C₆H₅CH₂OH on this column, by ¹H NMR and mass spectral analysis.

Photochemistry of Dipalladium(I) Hexakis(methyl isocyanide) Hexafluorophosphate

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Received December 7, 1982

Summary: The photochemistry of [Pd₂^I(CNCH₃)₆]₂(PF₆) in the presence of halogen atom donors CX₄ (X = Cl, Br) is found to lead to halogen atom abstraction yielding

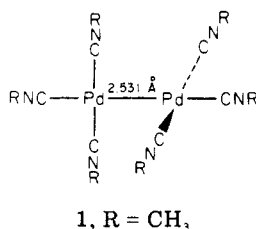
[Pd^{II}X(CNCH₃)₃] PF₆. Cross coupling of [•]Pd^I(CNCH₃)₃⁺ and [•]Pt^I(CNCH₃)₃⁺ radical fragments gives heteronuclear [PdPt(CNCH₃)₆]₂(PF₆) when the homonuclear species [Pd₂^I(CNCH₃)₆]₂(PF₆) and [Pt₂^I(CNCH₃)₆]₂(PF₆) are irradiated together. Homonuclear species are obtained when [PdPt(CNCH₃)₆]₂(PF₆) is irradiated. These results are interpreted in terms of the photogeneration of reactive 15 valence electron species [•]Pd^I(CNCH₃)₃⁺ via homolysis of the Pd-Pd bond in σ_b → σ* or dπ → σ* excited states. Quantum yields for the disappearance of [Pd₂^I(CNCH₃)₆]₂(PF₆) in the presence of CX₄ (X = Cl, Br) are high, Φ_{dis₃₁₃} = 0.42 (CCl₄) and 0.70 (CBr₄), suggesting efficient cleavage of a Pd-Pd bond in the excited state. UV photolysis of [Pd₂^I(CNCH₃)₆]₂(PF₆) in CH₃CN frozen solution at 150 K in an EPR cavity leads to the observation of a metal based radical with g ≈ 2.12.

We wish to report the first observation of photochemistry of a Pd-Pd metal-metal bond. The photochemistry of metal-metal bonds has been an area of intense interest.¹⁻³⁴ Complexes having metal-metal single bonds, no-

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tably $M_2(CO)_{10}$ ($M = Mn, Re$) and related species, generally undergo photochemical M–M bond homolysis proceeding from $d\pi \rightarrow \sigma^*$ or $\sigma_b \rightarrow \sigma^*$ lowest excited states to yield reactive 17-electron metal-based radicals, of which $\cdot M(CO)_5$ is an example. We have undertaken the study of the photochemistry of the dipalladium(I) isocyanide complex $[Pd_2^I(CNCH_3)_6] \cdot 2(PF_6)$, first prepared by Balch and co-workers in 1975.³⁵

The structure of $[Pd_2^I(CNCH_3)_6] \cdot 2(PF_6)$, **1** has been demonstrated³⁶ to contain two locally square-planar coordinated Pd(I) centers separated by 2.531 (9) Å. The overall symmetry of the complex approximates D_{2d} . The Pd–Pd separation is consistent with a Pd–Pd single bond.^{35–37}



The salient features of the bonding in $[Pd_2^I(CNCH_3)_6] \cdot 2(PF_6)$ can be understood from the combination of two T-shaped, d^9 , 15 valence electron fragments to form σ_b ($2a_1$) and σ^* ($2b_2$) molecular orbitals, of which only the former is occupied.^{35,37} Photoexcitation of $[Pd_2^I(CNCH_3)_6] \cdot 2(PF_6)$ is expected therefore to produce a $\sigma_b \rightarrow \sigma^*$ excited state which is unstable with respect to the formation of $\cdot Pd^I(CNCH_3)_3^+$ radical fragments. It is important to note that prior studies^{1–34} of the photochemistry of M–M single bonds have been concerned only with systems such as $M_2(CO)_{10}$ ($M = Mn, Re$), $Co_2(CO)_8$, and $M_2(\eta^5-C_5H_5)_2(CO)_6$ ($M = Mo, W$) which yield 17-electron radicals upon photolysis. Part of the impetus for the present study, therefore, is the examination of the reactivity of highly coordinatively unsaturated 15-electron radical fragments: $\cdot Pd^I(CNCH_3)_3^+$.

The electronic absorption spectrum of $[Pd_2^I(CNCH_3)_6] \cdot 2(PF_6)$ exhibits a strong band in the ultraviolet, $\lambda_{max} = 307$ nm ($\epsilon = 1.0 \times 10^4$ L m^{-1} cm^{-1}), and is shown in Figure 1. This band is assigned to $\sigma_b \rightarrow \sigma^*$ excitation on the basis of our photochemical results presented below. Irradiation into this band, $\lambda_{excit} = 313$ nm,⁴⁰ in solutions which are 0.02 M $[Pd_2^I(CNCH_3)_6] \cdot 2(PF_6)$ and 1.0 M in CX_4 ($X = Cl, Br$) leads cleanly to halogen atom abstraction and the formation of $[Pd^{II}X(CNCH_3)_3](PF_6)$. The progress of the abstraction reaction is conveniently monitored by infrared spectroscopy.⁴¹ Complex **1** exhibits an intense IR band at $\nu(CN) = 2236$ cm^{-1} which loses intensity during the photolysis of solutions containing CX_4 ($X = Cl, Br$). Simultaneously, a new band grows in at $\nu(CN) = 2284$ cm^{-1} (X

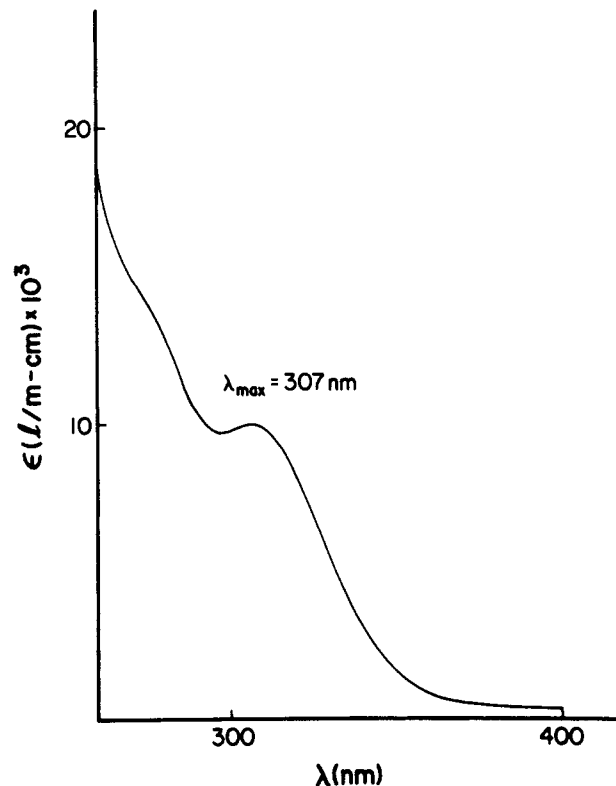


Figure 1. Electronic absorption spectrum of $[Pd_2(CNCH_3)_6] \cdot 2(PF_6)$ in CH_2Cl_2 solution.

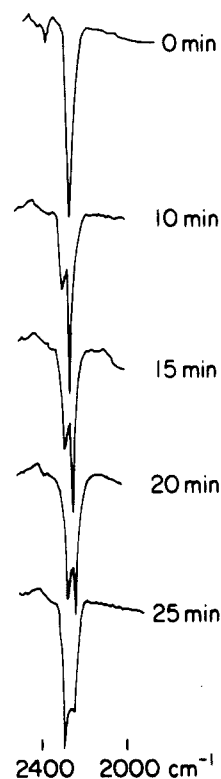


Figure 2. Change in the $C\equiv N$ stretching region of the infrared spectrum of a 0.02 M $[Pd_2(CNCH_3)_6] \cdot 2(PF_6)$ /1.0 M CCl_4 acetonitrile solution as a function of photolysis time at 313 nm.

$X = Cl$) and 2278 cm^{-1} ($X = Br$). The change in the infrared spectrum of $[Pd_2(CNCH_3)_6] \cdot 2(PF_6)$ in the presence of 1.0 M CCl_4 is given as a function of photolysis time in Figure 2. The appearance of a single new band in the IR spectra of photolyzed solutions indicates clean conversion to a single photoproduct. In order to identify the

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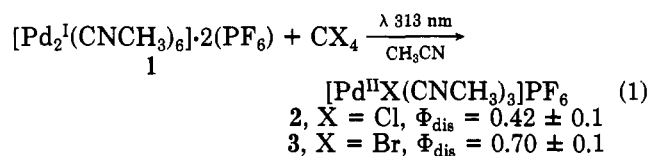
(40) Irradiation sources were either a Xenon Corp. 200-W Xe arc lamp or Oriol 6141 1000-W Xe arc lamp using an Oriol 7240 monochromator with a 0.1-mm slit width. Bulk photolyses were effected with an Ace/Hanovia 550-W medium-pressure Hg lamp.

(41) Typically, photolysis solutions were 0.02 M $[Pd_2(CNCH_3)_6] \cdot 2(PF_6)$ and 1.0 M CX_4 ($X = Cl, Br$) in acetonitrile which was previously distilled over P_2O_5 under N_2 . Solutions were transferred into 0.2-mm CaF_2 solution IR cells in an inert-atmosphere box. Infrared spectra were recorded on a Perkin-Elmer 700 or Nicolet 5-MX Fourier Transform spectrophotometer.

photoproduct definitively, we have carried out exhaustive bulk photolyses. $[\text{PdX}(\text{CNCH}_3)_3]\text{PF}_6$ ($\text{X} = \text{Cl}, \text{Br}$) is the sole product obtained from photolyzed solutions containing CCl_4 or CBr_4 , respectively, based on IR, NMR, and microanalytical data.⁴² The halogen abstraction must proceed by a photochemical pathway. We see no evidence for a thermal reaction between $[\text{Pd}_2^{\text{I}}(\text{CNCH}_3)_6]\cdot 2(\text{PF}_6)$ and CCl_4 when solutions identical with those used in the photochemical studies are refluxed for up to 6 h. We do, however, observe a slow thermal reaction between 1 and CBr_4 under the same conditions.

The participation of $\cdot\text{Pd}^{\text{I}}(\text{CNCH}_3)_3^+$ radicals in the observed photochemistry is strongly suggested by the results of a cross-coupling experiment. Photolysis of a mixture of the two homonuclear dimers $[\text{Pd}_2^{\text{I}}(\text{CNCH}_3)_6]\cdot 2(\text{PF}_6)$ and $[\text{Pt}_2^{\text{I}}(\text{CNCH}_3)_6]\cdot 2(\text{PF}_6)$ ³⁸ gives the heteronuclear $[\text{PdPt}(\text{CNCH}_3)_6]\cdot 2(\text{PF}_6)$.³⁸ This photochemical cross-coupling reaction is conveniently monitored by ¹⁹⁵Pt NMR spectroscopy. The platinum dimer, $[\text{Pt}_2^{\text{I}}(\text{CNCH}_3)_6]\cdot 2(\text{PF}_6)$ exhibits a ¹⁹⁵Pt NMR signal at $\delta -2916$ relative to K_2PtCl_4 . The mixed-metal dimer $[\text{PdPt}(\text{CNCH}_3)_6]\cdot 2(\text{PF}_6)$ has been independently prepared by an established chemical synthesis,³⁸ and it exhibits a ¹⁹⁵Pt NMR signal at $\delta -2833$ relative to K_2PtCl_4 . Significantly, the photolysis of an equimolar mixture of the two homonuclear dimers in acetonitrile solutions is accompanied by loss in intensity at $\delta -2916$ and concomitant increase in intensity at $\delta -2833$ relative to K_2PtCl_4 . Similarly, irradiation of solutions originally containing only the mixed-metal dimer $[\text{PdPt}(\text{CNCH}_3)_6]\cdot 2(\text{PF}_6)$ cleanly yields homonuclear $[\text{Pt}_2(\text{CNCH}_3)_6]\cdot 2(\text{PF}_6)$, as evidenced by the growth of a ¹⁹⁵Pt signal at $\delta -2916$. These results suggest that $\cdot\text{Pd}^{\text{I}}(\text{CNCH}_3)_3^+$ and $\cdot\text{Pt}^{\text{I}}(\text{CNCH}_3)_3^+$ radical fragments are formed upon photochemical homolysis of Pd-Pd, Pt-Pt, and Pd-Pt bonds in the dimetallic hexakis(isocyanide) complexes used in this study and that the lifetimes of these radicals are sufficient for cross coupling between dimers to occur. The cross-coupling experiments have also been followed by ¹H NMR spectroscopy at 200 MHz of the isocyanide methyl resonances. The results of our ¹H NMR studies entirely support the ¹⁹⁵Pt NMR data, and further details will be provided in the full paper. We note that all cross-coupling photolyses were done at 0 °C and that no evidence for thermal cross coupling at 25 °C is observed over periods of weeks.

The efficiencies for halogen atom abstractions by photogenerated $\cdot\text{Pd}^{\text{I}}(\text{CNCH}_3)_3^+$ radicals are high. Quantum yields for disappearance of $[\text{Pd}_2(\text{CNCH}_3)_6]\cdot 2(\text{PF}_6)$, $\Phi_{\text{dis}313}$, are 0.42 ± 0.1 and 0.70 ± 0.1 for reactions with CCl_4 and CBr_4 , respectively (eq 1). The high quantum yields for



halogen atom abstraction suggest the efficient homolysis of the Pd-Pd bond is responsible for the observed photochemistry. An important line of investigation therefore is the direct observation of $\cdot\text{Pd}^{\text{I}}(\text{CNR})_3^+$ radicals obtained

(42) $[\text{Pd}^{\text{II}}\text{Cl}(\text{CNCH}_3)_3]\text{PF}_6$: IR $\nu(\text{CN})$ 2284 cm^{-1} (CH_2Cl_2); ¹H NMR $\delta(\text{CH}_3)$ 3.49, (s, CD_3CN). Anal. Calcd: C, 17.56; H, 2.19; N, 10.25. Found: C, 17.80; H, 2.21; N, 10.35.

$[\text{Pd}^{\text{II}}\text{Br}(\text{CNCH}_3)_3]\text{PF}_6$: IR $\nu(\text{CN})$ 2278 cm^{-1} (CH_2Cl_2); ¹H NMR $\delta(\text{CH}_3)$ 3.39, (s, CD_3CN). Anal. Calcd: C, 15.85; H, 1.98; N, 9.26. Found: C, 16.04; H, 2.02; N, 9.38.

(43) Quantum yields were measured at 313 nm by ferrioxalate actinometry or by direct comparison with 0.01 M $\text{Mn}_2(\text{CO})_{10}$ in neat CCl_4 solution assuming $\Phi_{\text{dis}313} = 0.48$.¹¹

by homolysis of the Pd-Pd bond in 1. UV photolysis of frozen acetonitrile solutions of 1 in an EPR cavity at 150 K causes the appearance of an intense EPR signal with an apparent $g_{\text{iso}} = 2.12$, consistent with a metal-based radical. The signal is quenched by melting the matrix or discontinuing photolysis. The EPR results provide additional support for the notion that photochemical Pd-Pd bond homolysis of 1 precedes the observed halogen atom abstraction photochemistry.

Our results suggest that photolysis of 1 leads to homolysis of the $\text{Pd}^{\text{I}}-\text{Pd}^{\text{I}}$ bond to give two 15-electron $d^9 \cdot \text{Pd}^{\text{I}}(\text{CNCH}_3)_3^+$ fragments which are capable of reacting in a one-electron sense with halocarbons to give $\text{Pd}^{\text{II}}\text{X}(\text{CNCH}_3)_3^+$. The photogeneration of reactive organometallic fragments has recently found application in the activation of aliphatic C-H bonds.⁴⁴ Reactive photogenerated species such as $\cdot\text{Pd}^{\text{I}}(\text{CNR})_3^+$ may find significant applications in the activation of small molecules or C-H bonds. Further studies in these laboratories are being conducted along these lines. In particular, the 15 valence electron species $\cdot\text{Pd}^{\text{I}}(\text{CNCH}_3)_3^+$ has the clear potential to participate in three-electron activations of substrates such as allylic systems, NO, and alkylidynes.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research. This work was also supported in part by the Purdue Research Foundation. The assistance of Mr. John Copeland in the design and construction of the medium-pressure mercury lamp and the assistance of Mr. William Kennedy in obtaining EPR spectra of UV photogenerated radicals are gratefully acknowledged. The experimental assistance of Mr. David Whittern in obtaining the ¹⁹⁵Pt NMR and 200-MHz ¹H NMR spectra is also gratefully acknowledged. The Varian XL-200 spectrometer was purchased with funds from NSF Grant CHE-8004246. This support is gratefully acknowledged.

Registry No. 1, 56116-48-4; 2, 69108-81-2; 3, 69108-67-4; $[\text{PdPt}(\text{CNCH}_3)_6]\cdot 2(\text{PF}_6)$, 60767-38-6; Pd, 7440-05-3.

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Organic Sonochemistry. Ultrasonic Acceleration of the Hydrosilation Reaction¹

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Received October 20, 1982

Summary: Sonic waves permit the platinum-catalyzed addition of Si-H bonds across C=C and C≡C bonds at ~30 °C in high yields.

The first examples of platinum-catalyzed hydrosilations were described by Wagner and Strother.² In that work the addition reactions were performed at 45–115 psi at temperatures of 100–300 °C using, in most cases, trichlorosilane, as well as dichlorosilane, triethoxysilane, and ethyldichlorosilane, on a series of terminal alkenes. Subsequent work by Wagner and others demonstrated that heterogeneous platinum catalysts accelerated a variety of