The Photochemistry of Palladium and Platinum Homo- and Heteronuclear Metal–Metal σ-Bonds: Efficient Photogeneration of 15-Electron Radicals

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Abstract: The photochemistry of homo- and heteronuclear palladium(I) and platinum(I) hexakis(methyl isocyanide) dimers, $MM'(CNMe)_6^{2+}$ (M = M' = Pd, Pt; M = Pd, M' = Pt), has been examined. The primary photoprocess of these complexes is homolysis of their M–M σ-bonds to give reactive 15 valence electron $\cdot M(CNMe)_3^+$ radicals. The metal–ligand bonds of the ground-state $MM'(CNMe)_6^{2+}$ complexes are labile in acetonitrile solutions where thermal redistribution of isocyanide ligands between $Pd_2(CNCD_3)_6^{2+}$ and $Pt_2(CNCH_3)_6^{2+}$ gives $[Pd_2(CNCD_3)_x(CNCH_3)_{6-x}]^{2+}$. Photolysis of the homonuclear complexes $Pd_2(CNMe)_6^{2+}$ and $Pt_2(CNMe)_6^{2+}$ gives heteronuclear $PdPt(CNMe)_6^{2+}$ as monitored by ^{195}Pt NMR. Reverse crossovers from $PdPt(CNMe)_6^{2+}$ give the homonuclear complexes as observed by ^{195}Pt and ^1H NMR. Photogenerated $\cdot M(CNMe)_3^+$ radicals undergo Cl and Br atom abstractions from CX_4 (X = Cl, Br) to form as the only photoproducts $MX(CNMe)_3^+$ (M = Pd, Pt; X = Cl, Br). Limiting quantum yields for Cl-atom abstractions from CCl_4 are 0.40 ± 0.05, 0.12 ± 0.01, and 0.05 ± 0.01 for $Pd_2(CNMe)_6^{2+}$, $PdPt(CNMe)_6^{2+}$, and $Pt_2(CNMe)_6^{2+}$, respectively. The relative Cl-abstraction reactivity of photogenerated $\cdot Pt(CNMe)_3^+$ and $\cdot Pd(CNMe)_3^+$, k_{Pt}/k_{Pd}, was found to be 4.6 ± 0.2 by a kinetic competition experiment employing $PdPt(CNMe)_6^{2+}$ photolysis. The lower quantum yield of Cl abstraction by $Pt_2(CNMe)_6^{2+}$ together with higher reactivity of $\cdot Pt(CNMe)_3^+$ radicals is interpreted in terms of excited-state decay channels.

The photochemistry of metal–metal σ-bonds has been an area of intense interest in recent years.[1-37] The σ → σ* or dπ → σ* excited states of M–M bonded species generally are dissociative with respect to the formation of reactive organometallic free radicals. Recently, the photogeneration of reactive organometallic species has found application in the formation of highly active catalysts[38] and in the activation of aryl and aliphatic C–H bonds.[44-47] Reactive photogenerated organometallic intermediates can be understood to originate from either of two principal elementary photoprocesses. The first involves labilization and loss of ligands from excited states with significant M–L antibonding character. This process leads to coordinatively unsaturated species which may react with substrates. This general sequence of reactions is apparently operative in the activation of C–H bonds of saturated hydrocarbons upon photochemical reductive elimination of H_2 from $(\eta^5\text{-}C_5Me_5)(PMe_3)IrH_2$,[44] or photochemical CO loss from $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$.[45] The second elementary photoprocess, which is observed for di- and polynuclear metal complexes, is M–M bond homolysis. The σ → σ* or dπ → σ* excited states of binuclear complexes may undergo metal–metal bond homolysis giving free radicals. The radicals can be reactive toward ligand substitution or toward radical abstractions. The σ → σ* photochemistry of $M_2(CO)_{10}$ (M = Mn, Re), (η^5-

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$C_5H_5)_2M_2(CO)_6$ (M = Mo, W), $Co_2(CO)_8$, and related isoelectronic complexes has been particularly well studied.

We report herein our studies of the photochemistry of unsupported homo- and heteronuclear metal–metal bonds between platinum and palladium atoms. The binuclear hexakis(isocyanide) complexes employed in this study possess the general structure I.[39,40] The bonding in these M_2L_6 systems can be understood from

I

(M = M' = Pd, Pt; M = Pd, M' = Pt)
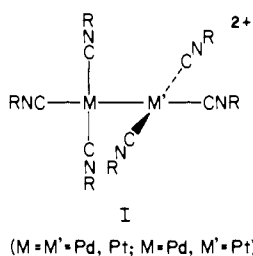
the combination of two T-shaped, d^9, 15 valence electron ML_3 fragments to form σ_b ($2a_1$) and σ^* ($2b_2$) molecular orbitals, of which only the former is occupied.[40,41] Photoexcitation of the M_2L_6 complexes therefore is expected to yield $\sigma \rightarrow \sigma^*$ excited states which may homolytically cleave to two d^9, 15-electron, $\cdot ML_3^+$ radical fragments. We note that all prior studies of the photochemistry of M–M σ-bonds have been concerned only with systems such as $M_2(CO)_{10}$ (M = Mn, Re), $Co_2(CO)_8$, and $M_2(\eta^5\text{-}C_5H_5)_2(CO)_6$ (M = Mo, W) which yield 17-electron fragments upon photolysis. Studies of d^9 M_2L_6 complexes are therefore of particular interest. The formally 15-electron $\cdot ML_3^+$ (M = Pd, Pt) species are in principle capable of reacting through both channels available to photogenerated organometallic intermediates since they are both coordinatively unsaturated and free radical in nature. A preliminary report of this work has appeared.[52]

Experimental Section

Materials. The compounds $[Pd_2(CNMe)_6][PF_6]_2$, $[PdPt(CNMe)_6][PF_6]_2$, and $[Pt_2(CNMe)_6][BF_4]_2$ were prepared by established methods.[42,43] Methyl isocyanide was prepared by the dehydration of *N*-methylformamide following the procedure of Werner et al.[50] Unless otherwise noted all solvents were dried and distilled under an N_2 atmosphere and all manipulations were performed under N_2 with either Schlenk techniques or a Vacuum Atmospheres Model HE-43-2 Dry Lab equipped with Model HE 493 Dri-Train. CCl_4 (Mallinckrodt, Spectrometric Grade) and CBr_4 (Matheson, Coleman and Bell) were used as received.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 700, Perkin-Elmer 1420 with Model 3600 data station or Nicolet 5-MX FT-IR with 0.2 or 0.05 mm CaF_2 solution IR cells. ^{1}H NMR spectra were recorded on either a Perkin-Elmer R32 90 MHz, Varian XL 200, or Nicolet NT 470 spectrometer. All [195]Pt NMR spectra were recorded on the Varian XL-200 instrument generally with 0.05 M solutions.

Photolysis samples were degassed in 3 freeze–pump–thaw cycles and then placed under N_2. Concentrations of complexes were 0.02 M in CH_2Cl_2 or CH_3CN. Solutions were photolyzed in 5- or 10-mm NMR tubes at 0 °C. [195]Pt NMR spectra of $[Pt_2(CNMe)_6][BF_4]_2$ in acetonitrile-d_3 were recorded at ambient temperature, and chemical shifts are reported relative to external K_2PtCl_4 in KCl/D_2O solution. UV–vis spectra were recorded on a Hewlett-Packard 8450A spectrophotometer with 1-cm evacuable quartz cells.

Lamps used for photolysis included a Xenon Corp. 150 W Xe arc lamp equipped with an Oriel Corp. 313-nm interference filter, an Oriel 6141 1000 W Xe arc lamp fitted with an Oriel 7240 monochromator at a 0.1-mm slit width, or for bulk photolyses, an Ace/Hanovia 550 W medium-pressure Hg lamp. All photolyses were performed at 0 °C.

Quantum Yields. Quantum yields for halogen atom abstraction by $[Pd_2(CNMe)_6][PF_6]_2$, $[PdPt(CNMe)_6][PF_6]_2$, and $[Pt_2(CNMe)_6][BF_4]_2$ were determined by two different methods.

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Table I. Electronic Absorption Spectral Data for Pd, Pt, and Pd–Pt Isocyanide Complexes

complex	solvent	λ_{max}(nm)	ϵ (M^{-1} cm^{-1})
$[Pd_2(CNMe)_6][PF_6]_2$	CH_2Cl_2	307	9 900
	CH_3CN	305	11 100
	CH_3SOCH_3	306	12 100
$[PdPt(CNMe)_6][PF_6]_2$	CH_2Cl_2	294	6 300
	CH_3CN	295	6 600
	CH_3SOCH_3	296	7 200
$[Pt_2(CNMe)_6][BF_4]_2$	CH_2Cl_2	297	4 500
	CH_3CN	296	4 350
	CH_3SOCH_3	298	6 000
$[PdCl(CNMe)_3][PF_6]$	CH_3CN	299	1 010
$[PdBr(CNMe)_3][PF_6]$	CH_3CN	230	7 000
$[PtCl(CNMe)_3][BF_4]$	CH_3CN	264	3 300
$[PtBr(CNMe)_3][BF_4]$	CH_3CN	266	4 600

Method 1: UV–vis Detection. Acetonitrile solutions which were between 5×10^{-5} and 1×10^{-4} M in metal complex and between 10^{-5} and 10^{-1} M in CCl_4 were prepared in evacuable 1-cm UV–vis quartz cells.

Samples were irradiated by an Oriel 6141 1000-W Xe arc lamp through a water IR filter and an Oriel 7240 monochromator at 0.1-mm slit width. All photolyses were performed at 313 nm at 0 °C. Quantum yields were determined vs. a ferrioxalate actinometer. Alternatively, quantum yields at 313 nm were determined relative to 1.0×10^{-5} M $Mn_2(CO)_{10}$ in neat CCl_4, using $\Phi_{313} = 0.48$ for the disappearance of $Mn_2(CO)_{10}$.[11] In all cases, samples were at or below 1 absorbance unit. Hence, quantum yields for disappearance, Φ_{dis}, of $[MM'(CNMe)_6]^{2+}$ (M = M' = Pd, Pt; M = Pd, M' = Pt) were calculated in terms of the quantum yield for the actinometer, Φ_{act}, using the following equation

$$\Phi_{dis} = \Phi_{act} \frac{(\Delta A^{\lambda_{max}}/\epsilon)}{(\Delta A_{act}^{\lambda_{max}}/\epsilon_{act})} \frac{t_{act}(1 - 10^{-A_{act}^{\lambda_{irr}}})}{t(1 - 10^{-A^{\lambda_{irr}}})}$$

where $\Delta A^{\lambda_{max}} \equiv$ change in absorbance at λ_{max} for the absorbing species, $t \equiv$ irradiation time, $\epsilon \equiv$ extinction coefficient at λ_{max}, and $A^{\lambda_{irr}} \equiv$ absorbance at the wavelength of irradiation. The equation above is not reliable for large changes in absorbance. Therefore, all quantum yields are based on total absorbance changes of <0.15 A. Data for quantum yields were generally obtained over the first several minutes of photolysis. Average light intensities at 313 nm were $I_a = 1.8 \times 10^7$ einstein/s.

Method 2: IR Detection. Acetonitrile solutions which were 0.02 M in metal complex and between 0.02 and 3 M in CCl_4 were prepared and freeze–pump–thaw degassed on a high-vacuum line. The solutions were then transferred to 0.05 or 0.2 mm CaF_2 solution IR cells. Samples were photolyzed in the IR cells and spectra recorded over the course of photolysis, monitoring the intense MeNC $\nu(C\equiv N)$ at $\sim$2230–2280 cm^{-1}. Quantum yields at 313 nm were determined relative to 5×10^{-3} M $Mn_2(CO)_{10}$ in neat CCl_4, monitoring $\nu(CO)$ of $Mn_2(CO)_{10}$. In all cases, samples were at or above 2.5 absorbance units at 313 nm and no corrections for differential absorbance were applied.

Metal–Metal Crossover Experiments. Crossover between $[Pd_2(CNMe)_6][PF_6]_2$ and $[Pt_2(CNMe)_6][BF_4]_2$ was monitored by [195]Pt NMR. Solutions were 0.025 M in the two homonuclear dimers and were prepared as CH_3CN/CD_3CN solutions. [195]Pt NMR spectra were recorded periodically over the course of 1 h of photolysis at 0 °C. The appearance of $[PdPt(CNMe)_6]^{2+}$ was confirmed by comparison to an authentic sample. [195]Pt NMR chemical shifts of $[Pt_2(CNMe)_6]^{2+}$ and $[PdPt(CNMe)_6]^{2+}$ are given in Table II.

Reverse crossover experiments employed 0.05 M CD_3CN solutions of the $[PdPt(CNMe)_6][BF_4]_2$ and were monitored by [195]Pt and 200-MHz ^{1}H NMR. Samples were photolyzed for 1 h at 0 °C. Spectra were recorded at 15-min intervals. In [195]Pt NMR experiments, the appearance of $[Pt_2(CNMe)_6]^{2+}$ was observed. In ^{1}H NMR experiments, the appearance of both $[Pt_2(CNMe)_6]^{2+}$ and $[Pd_2(CNMe)_6]^{2+}$ was observed. ^{1}H NMR data for the complexes are presented in Table II.

Metal–Ligand Crossover Experiments. Crossover between $[Pd_2(CN-CD_3)_6][PF_6]_2$ and $[Pt_2(CNCH_3)_6][BF_4]_2$ was monitored by 200-MHz ^{1}H NMR. The methyl-d_3 isocyanide was prepared by the method of Jackson and McKusick.[53] A sample of $[Pd_2(CNCD_3)_6][PF_6]_2$ was prepared by substituting methyl-d_3 isocyanide in the usual preparation for the proteo material.[42,43]

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Table II. ^{1}H, ^{195}Pt NMR, and IR Spectral Data for Pd, Pt, and Pd–Pt Isocyanide Complexes

complex	H^1 NMR^a (ppm)	^{195}Pt NMR^b (ppm)	ν(CN) (cm^{-1})^c
[Pd$_2$(CNMe)$_6$][PF$_6$]$_2$	δ 3.47 (s, 18 H)		2236
[PdPt(CNMe)$_6$][PF$_6$]$_2$	δ 3.55 (m, J_{Pt-H} = 18 Hz, 6 H), 3.44 (s, 9 H), 3.38 (m, 3 H)	δ –2833	2231
[Pt$_2$(CNMe)$_6$][BF$_4$]$_2$	δ 3.51 (m, J_{Pt-H} = 16 Hz, 12 H), 3.33 (m, 6 H)	δ –2916	2242
[PdCl(CNMe)$_3$][PF$_6$]	δ 3.56 (t, J_{N-H} = 2.4 Hz, 6 H), 3.50 (t, J_{N-H} = 2.6 Hz, 3 H)		2284
[PdBr(CNMe)$_3$][PF$_6$]	δ 3.56 (t, J_{N-H} = 2.4 Hz, 6 H), 3.48 (t, J_{N-H} = 2.5 Hz, 3 H)		2278
[PtCl(CNMe)$_3$][BF$_4$]	δ 3.60 (t, J_{N-H} = 2.7 Hz, 6 H), 3.57 (t, J_{N-H} = 2.5 Hz, 3 H)	δ –2682	2283
[PtBr(CNMe)$_3$][BF$_4$]	δ 3.61 (t, J_{N-H} = 2.6 Hz, 6 H), 3.55 (t, J_{N-H} = 2.5 Hz, 3 H)	δ –2854	2278

^{a}^{1}H NMR chemical shifts relataive to internal Me$_4$Si. ^{b}^{195}Pt NMR chemical shifts relative to external K$_2$PtCl$_4$/KCl. ^{c}All spectra recorded in CH$_3$CN solution.

A solution 0.02 M in [Pd$_2$(CNCD$_3$)$_6$][PF$_6$]$_2$ and 0.02 M in [Pt$_2$(CN-CH$_3$)$_6$][BF$_4$]$_2$ was prepared in 0.5 mL of acetonitrile-d_3 in a 5-mm NMR tube. The ^{1}H NMR spectrum was compared with that of similarly prepared acetonitrile-d_3 solutions of 0.02 M [Pd$_2$(CNCD$_3$)$_6$][PF$_6$]$_2$ alone and 0.02 M [Pt$_2$(CNCH$_3$)$_6$][BF$_4$]$_2$ alone.

Bulk Photolyses. Acetonitrile solutions 0.02 M in [M$_2$(CNMe)$_6$]$^{2+}$ (M = Pd, Pt) and 1 M in CCl$_4$ or CBr$_4$ were photolyzed to completion, as monitored by IR. The solution volume was then reduced and diethyl ether added to initiate precipitation. The sample solution was then cooled to –25 °C. the resulting white crystalline solids were filtered and dried in vacuo.

[PdCl(CNMe)$_3$][PF$_6$]: IR (CH$_3$CN) ν(CN) 2284 cm^{-1}; ^{1}H NMR (CD$_3$CN) δ 3.50 (m, 3 H), δ 3.56 (m, 6 H). Anal. Calcd: C, 17.58; H, 2.21; N, 10.25. Found: C, 18.08; H, 2.21; N, 10.35.

[PtCl(CNMe)$_3$][BF$_4$]: IR (CH$_3$CN) ν(CN) 2283 cm^{-1}; ^{1}H NMR (CD$_3$CN) δ 3.60 (m, 9 H); ^{195}Pt NMR (CD$_3$CN) δ –2682. Anal. Calcd: C, 16.36; H, 2.05; N, 9.54; Cl, 8.05. Found: C, 16.60; H, 2.09; N, 9.43; Cl, 7.95.
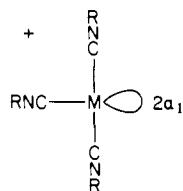
[PdBr(CNMe)$_3$][PF$_6$]: IR (CH$_3$CN) ν(CN) 2278 cm^{-1}; ^{1}H NMR (CD$_3$CN) δ 3.48 (m, 3 H), δ 3.56 (m, 6 H). Anal. Calcd: C, 15.86; H, 2.00; N, 9.25; Br, 17.58. Found: C, 16.83; H, 2.96; N, 9.60; Br, 16.78.

[PtBr(CNMe)$_3$][BF$_4$]: IR (CH$_3$CN) ν(CN) 2278 cm^{-1}; ^{1}H NMR (CD$_3$CN) δ 3.55 (m, 3 H), δ 3.61 (m, 6 H); ^{195}Pt-NMR (CD$_3$CN) δ –2854. Anal. Calcd: C, 14.86 H, 1.87; N, 8.66; Br, 16.48. Found: C, 15.76; H, 2.21; N, 9.30; Br, 14.70.

Results and Discussion

A. Electronic Absorption Spectra. The homo- and heteronuclear complexes of this study, MM′(CNMe)$_6$$^{2+}$ (M = M′ = Pd, Pt; M = Pd, M′ = Pt), all exhibit intense electronic absorptions in the vicinity of 300 nm. For example, Pd$_2$(CNMe)$_6$$^{2+}$ has an absorption feature with λ_{max} = 307 nm, ϵ = 11,100 M^{-1} cm^{-1} in acetonitrile solution at 25 °C. Absorption maxima vary little through the series and appear at 295 and 296 nm for PdPt-(CNMe)$_6$$^{2+}$ and Pt$_2$(CNMe)$_6$$^{2+}$, respectively. The molar extinction coefficients range from ϵ ~ 11 000 for Pd$_2$(CNMe)$_6$$^{2+}$ to ϵ ~ 5 000 for Pt$_2$(CNMe)$_6$$^{2+}$. There is essentially no dependence of λ_{max} on solvent for the three binuclear complexes. There is also relatively little intensity dependence on solvent. Electronic absorption spectral data for CH$_2$Cl$_2$, CH$_3$CN, and Me$_2$SO solutions of the complexes are presented in Table I. None of the complexes of this study have been observed to luminesce either in solution or in the solid state.

The generally intense ultraviolet absorptions for the MM′-(CNMe)$_6$$^{2+}$ complexes are assigned to $\sigma \rightarrow \sigma^*$ excitation. The bonding in these complexes can be understood from the combination of two T-shaped, d^9, 15 valence electron ·M(CNMe)$_3$$^+$ fragments and has been considered in some detail by Hoffman and Hoffmann.[41] The T-shaped ·ML$_3$ radical can be derived by removing a ligand, along the y axis, from a square-planar ML$_4$ system. This leaves a singly occupied hybrid orbital (2a$_1$) of metal s, p, and d$_{x^2-y^2}$ character. Symmetric and antisymmetric combinations of these hybrids from two fragments give the σ(2a$_1$) and

$$
\begin{array}{c}
+ \quad
\begin{array}{c}
R \\ N \\ C \\ | \\
RNC\!-\!M\!-\!\!\bigcirc \quad 2a_1 \\
| \\ C \\ N \\ R
\end{array}
\end{array}
$$

σ^*(2b$_2$) orbitals respectively of the binuclear M$_2$L$_6$ complex. We

note that in the electronic absorption spectra of the MM′-(CNMe)$_6$$^{2+}$ complexes of this study we do not observe lower energy d$\pi \rightarrow \sigma^*$ features which are generally seen for d^7–d^7, e.g., Mn$_2$(CO)$_{10}$, Re$_2$(CO)$_{10}$, and d^5–d^5, e.g., W$_2$Cp$_2$(CO)$_6$,[11] Mo$_2$Cp$_2$(CO)$_6$, systems. It is likely that d$\pi \rightarrow \sigma^*$ transitions occur at higher energies than $\sigma \rightarrow \sigma^*$ in our d^9–d^9 M$_2$L$_6$ systems. This is in accordance with the expected greater energy separation between a d$_{x^2-y^2}$ like HOMO and dπ orbitals of a d^9 T-shaped ·ML$_3$ fragment compared to the d$_{z^2}$ like HOMO and dπ orbitals of a d^7 square-pyramidal fragment such as ·Mn(CO)$_5$. The only calculations available at the present time which bear on this issue are extended Hückel calculations for the isoelectronic Rh$_2$Cl$_2$H$_4$$^{6-}$ ion.[41] These do suggest the totally bonding M–M σ-orbital lies above the corresponding π^* orbitals. The theoretical considerations agree well with our experimental observations. In particular, a $\sigma \rightarrow \sigma^*$ assignment of the observed optical transitions in the MM′(CNMe)$_6$$^{2+}$ (M = M′ = Pd, Pt; M = Pd, M′ = Pt) complexes is completely consistent with the very high observed extinction coefficients and the absence of solvent effects on the absorption energies.

B. Photochemical Lability of M–M Bonds. The metal–metal bonds of the MM′(CNMe)$_6$$^{2+}$ (M = M′ = Pd, Pt; M = Pd, M′ = Pt) complexes become extremely labile upon excitation into the $\sigma \rightarrow \sigma^*$ absorption bands. Evidence for the photochemical labilization of the M–M bonds is derived from the results of crossover experiments.

Photolysis of a mixture of the two homonuclear species Pd$_2$-(CNMe)$_6$$^{2+}$ and Pt$_2$(CNMe)$_6$$^{2+}$ gives heteronuclear PdPt-(CNMe)$_6$$^{2+}$. This crossover reaction has been monitored by ^{195}Pt NMR. The complex Pt$_2$(CNMe)$_6$$^{2+}$ exhibits a ^{195}Pt NMR signal at δ –2916 while the mixed-metal complex, PdPt(CNMe)$_6$$^{2+}$, exhibits a signal at δ –2833 relative to K$_2$PtCl$_4$. Significantly, photolysis of an equimolar mixture of the two homonuclear complexes is accompanied by a loss of intensity at δ –2916 and concomitant increase in intensity of one signal at δ –2833, corresponding to the formation PdPt(CNMe)$_6$$^{2+}$. This result implies the only new Pt-containing product arising from the photolysis of Pt$_2$(CNMe)$_6$$^{2+}$ in the presence of Pd$_2$(CNMe)$_6$$^{2+}$ is PdPt-(CNMe)$_6$$^{2+}$.

Reverse crossover experiments yield similar results and have been monitored by both ^{195}Pt and ^{1}H NMR. Relevant ^{195}Pt and ^{1}H NMR data for the homo- and heteronuclear complexes are given in Table II. The result of the reverse crossover experiment, beginning with PdPt(CNMe)$_6$$^{2+}$, as monitored by ^{195}Pt NMR is presented in Figure 1. Irradiation of PdPt(CNMe)$_6$$^{2+}$ in an NMR tube causes loss of intensity at δ –2833 while a solitary new signal at δ –2916 appears. This result suggests that the only Pt-containing photoproduct resulting from irradiation of the mixed-metal complex, PdPt(CNMe)$_6$$^{2+}$, is Pt$_2$(CNMe)$_6$$^{2+}$.

It is clear from our ^{1}H NMR studies at 200 MHz that Pd$_2$-(CNMe)$_6$$^{2+}$ is the only other photoproduct besides Pt$_2$(CNMe)$_6$$^{2+}$ which is obtained when PdPt(CNMe)$_6$$^{2+}$ is irradiated. The ^{1}H NMR spectra of the MM′(CNMe)$_6$$^{2+}$ (M = M′ = Pd, Pt; M = Pd, M′ = Pt) complexes at 25 °C appear in Figure 2. At 25 °C the two methyl isocyanide ligands coaxial with the Pd–Pd bond of Pd$_2$(CNMe)$_6$$^{2+}$ are equilibrated with the four equatorial ligands. This equilibration has been interpreted in terms of a unimolecular rearrangement.[40,43] We find, however, that Pd–CNMe bonds are exceedingly labile (vide infra), and a solvent-assisted bimolecular process cannot be dismissed. The platinum species Pt$_2$(CNMe)$_6$$^{2+}$

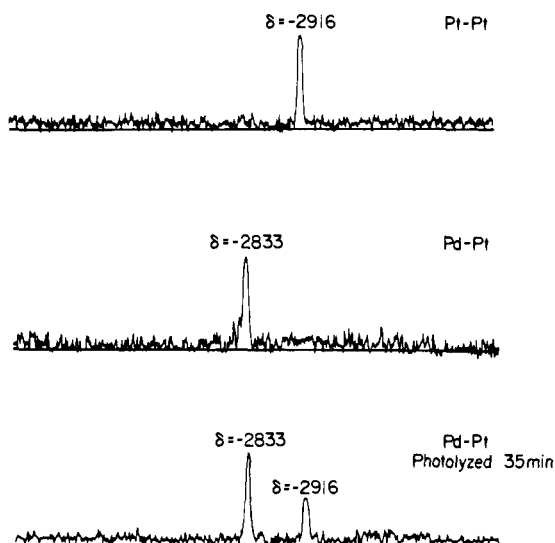**Figure 1.** ^{195}Pt NMR of Pt$_2$(CNMe)$_6^{2+}$ and PdPt(CNMe)$_6^{2+}$ before and after photolysis for 35 min. The appearance of a signal at δ -2916 corresponds to Pt$_2$(CNMe)$_6^{2+}$ arising from recombination of photogenerated $\cdot$Pt(CNMe)$_3^+$ radicals.
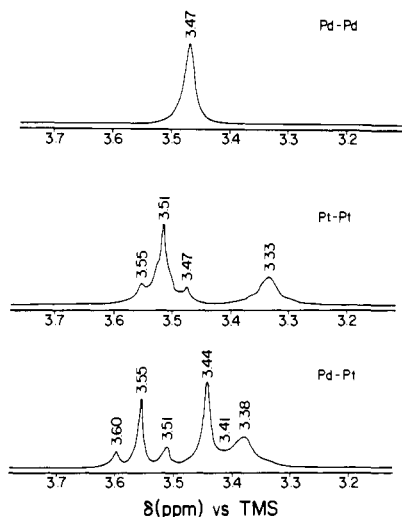

Figure 2. ^{1}H NMR spectra (200 MHz) of Pd$_2$(CNMe)$_6^{2+}$, PdPt-(CNMe)$_6^{2+}$, and Pt$_2$(CNMe)$_6^{2+}$ in CD$_3$CN at 25 °C.
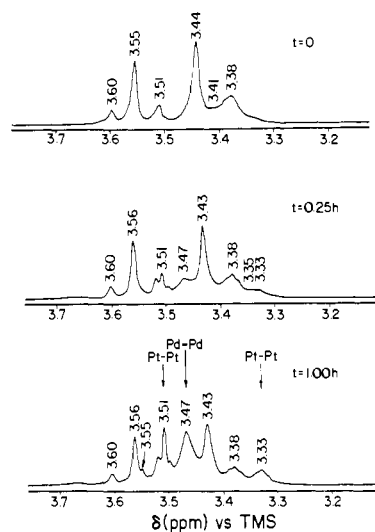

Figure 3. ^{1}H NMR spectra (200 MHz) of a photolyzed sample of PdPt(CNMe)$_6^{2+}$ as a function of photolysis time.

Figure 4. Change in C≡N stretching region of the IR spectrum accompanying photolysis of Pd$_2$(CNMe)$_6^{2+}$ at 313 nm. The peak at 2236 cm^{-1} corresponds to Pd$_2$(CNMe)$_6^{2+}$ and decreases in intensity as a single new peak at 2284 cm^{-1}, corresponding to PdCl(CNMe)$_3^+$ increases. Spectra were recorded every 30 s during photolysis.

exhibits separate axial and equatorial methyl isocyanide resonances at δ 3.33 and 3.51, respectively, with ^{195}Pt satellites. The ^{1}H NMR spectrum of the mixed-metal complex PdPt(CNMe)$_6^{2+}$ shows separate axial and equatorial methyl isocyanide resonances at δ 3.38 and 3.55, respectively. Moreover, these two signals must arise from the methyl isocyanides coordinated to the Pt atom as evidenced by the ^{195}Pt satellites. Interestingly, the methyl isocyanide ligands coordinated to the Pd atom are equivalent as evidenced by the signal at δ 3.44. These results suggest that a dynamic process is equilibrating axial and equatorial isocyanide ligands at the Pd half of PdPt(CNMe)$_6^{2+}$ while no such process is occurring at the Pt half of the complex at 25 °C. The key result in the present study is, however, the observation by ^{1}H NMR of photochemical cross-coupling of PdPt(CNMe)$_6^{2+}$. The changes in the 200-MHz ^{1}H NMR which accompany photolysis of PdPt(CNMe)$_6^{2+}$ are shown in Figure 3. After 15 min of photolysis, new signals can be discerned which result from crossovers. After 1 h of photolysis, it is clear that the homonuclear species Pd$_2$(CNMe)$_6^{2+}$ and Pt$_2$(CNMe)$_6^{2+}$ are the sole products of PdPt(CNMe)$_6^{2+}$ photolysis. The resulting product distribution is also essentially statistical, e.g., [Pd$_2^{2+}$]:[PdPt^{2+}]:[Pt$_2^{2+}$], ~1:2:1

after exhaustive photolysis. We note that all photochemical crossover experiments were done at 0 °C and that no evidence for thermal crossover at 25 °C can be observed, even over a period of several days. The results of our crossover experiments suggest that $\cdot$Pd(CNMe)$_3^+$ and $\cdot$Pt(CNMe)$_3^+$ radical fragments are formed upon photochemical homolysis of the Pd–Pd, Pt–Pt, and Pd–Pt bonds of the dimetallic hexakis(isocyanide) complexes. They further suggest that the lifetimes of these radicals are sufficient for cross coupling between M–M bonds to occur.

C. Photochemical Halogen Atom Abstraction. The radical nature of the $\cdot$M(CNMe)$_3^+$ fragments formed upon photolysis of the MM'(CNMe)$_6^{2+}$ (M = M' = Pd, Pt; M = Pd, M' = Pt) complexes is evidenced in halogen atom abstraction reactions. Excitation at 313 nm into the $\sigma \rightarrow \sigma^*$ absorption bands of the M–M bonded complexes in 1 M CX$_4$ (X = Cl, Br) acetonitrile solutions cleanly produces pseudo-square-planar mononuclear products, MX(CNMe)$_3^+$, according to eq 1. The course of these halogen atom abstractions is conveniently monitored by IR. For example, Pd$_2$(CNMe)$_6^{2+}$ displays a single sharp ν(CN) band at 2236 cm^{-1} in acetonitrile solution. During the photolysis of Pd$_2$(CNMe)$_6^{2+}$ in the presence of CCl$_4$ a single new band appears in the ν(CN) region at 2284 cm^{-1} corresponding to PdCl-(CNMe)$_3^+$. The changes in the IR spectrum which occur during photolysis of a 0.02 M Pd$_2$(CNMe)$_6^{2+}$, 1 M CCl$_4$ solution are shown in Figure 4. The photochemical Cl-atom abstraction is essentially complete after 3.5 min of broad-band irradiation with a 150-W Xe arc lamp. We note that no evidence for thermal Cl-atom abstraction can be observed when solutions identical with

Figure 5. Quantum yields of disappearance, Φ_d, of $MM'(CNMe)_6^{2+}$ (M = M' = Pd, Pt; M = Pd, M' = Pt) as a function of $[CCl_4]$. Concentrations of $MM'(CNMe)_6^{2+}$ were 5×10^{-5} or 1×10^{-4} m in acetonitrile solutions. All quantum yields were obtained at 313 nm at an average light intensity, $I_a = 1.8 \times 10^{-7}$ einstein/s.

those used in the photochemical studies are refluxed for 6 h. Completely analogous results are obtained when $Pt_2(CNMe)_6^{2+}$ is substituted for $Pd_2(CNMe)_6^{2+}$. The corresponding photochemical Br-atom abstractions from CBr_4 have also been examined. The principal photoproduct is $MBr(CNMe)_3^+$ (M = Pd, Pt). In the case of CBr_4, we do observe a slow thermal reaction with the $M_2(CNMe)_6^{2+}$ complexes.

In order to ascertain the nature of the photoproducts obtained by photolysis of $MM'(CNMe)_6^{2+}$ (M = Pd, M' = Pt; M = M' = Pd, Pt) in the presence of CX_4 (X = Cl, Br), exhaustive bulk photolyses were carried out and the products isolated and characterized. Microanalytical data for the $MX(CNMe)_3^+$ photoproducts are given in the Experimental Section. The analytical results are very satisfactory for $MCl(CNMe)_3^+$ (M = Pd, Pt). They are somewhat less satisfactory for the Br atom abstraction products, $MBr(CNMe)_3^+$. We and others[42] have noted a propensity of the Br derivatives to disproportionate to $M(CNMe)_4^{2+}$ and $M(CNMe)_2Br_2$. The slight impurities in the $MBr(CNMe)_3^+$ complexes which we have observed may be attributed in part to this disproportionation process.

The ^1H NMR data for the $MX(CNMe)_3^+$ photoproducts are consistent with their expected pseudo-square-planar geometries. Each of the photoproducts displays two methyl isocyanide resonances of relative intensity 2:1. The methyl resonances assigned to the isocyanide ligand trans to the halide appear at lower field. In these formally Pd(II) and Pt(II) complexes the two bond couplings of methyl isocyanide protons and nitrogen nuclei are also observable. Both the methyl isocyanide trans as well as the chemically equivalent pair mutually cis to the halide display $^2J_{N-H}$ ~ 2.5 Hz for all of the $MX(CNMe)_3^+$ (M = Pd, Pt; X = Cl, Br) photoproducts.

The IR spectra of the $MX(CNMe)_3^+$ photoproducts are surprisingly simple. The formally Pd(II) and Pt(II) photoproducts show only single $\nu(CN)$ bands in the region 2278–2284 cm^{-1}. We note that the formally Pd(I) and Pt(I) $M_2(CNMe)_6^{2+}$ precursor complexes also exhibit only one band in their IR spectra, although at least two are expected. Some asymmetry in the $\nu(CN)$ region for $Pd_2(CNMe)_6^{2+}$ is evident, however, in Figure 4, suggesting a near degeneracy of the CN stretching modes. This is an apparently general trend in the palladium and platinum isocyanide complexes of this study. All IR data as well as ^1H NMR and relevant ^{195}Pt NMR data are presented in Table II.

In order to determine the efficiencies of photochemical halogen atom abstractions, quantum yield studies were conducted. The quantum yield for disappearance of $Pd_2(CNMe)_6^{2+}$ at 313 nm, $\Phi_d{}^{313}$, in the presence of CCl_4 is relatively high and approaches a limiting value of 0.40 ± 0.05. The corresponding platinum complex, $Pt_2(CNMe)_6^{2+}$, is characterized by a much lower limiting quantum yield, $\Phi_d{}^{313}$, of 0.05 ± 0.01. Limiting quantum yields refer to conditions of high concentrations of CCl_4 of ~0.1 M, in acetonitrile solutions which were $0.5–1.0 \times 10^{-4}$ M in metal complex, $MM'(CNMe)_6^{2+}$. The mixed-metal complex $PdPt(CNMe)_6^{2+}$ reacts with a limiting quantum yield intermediate between the two homonuclear species, $\Phi_d{}^{313}$ ~ 0.12 ± 0.01. Quantum yields for disappearance of the three complexes have been examined further over the range of concentrations of CCl_4 from 10^{-1} to 10^{-5} M. The results of these studies are summarized
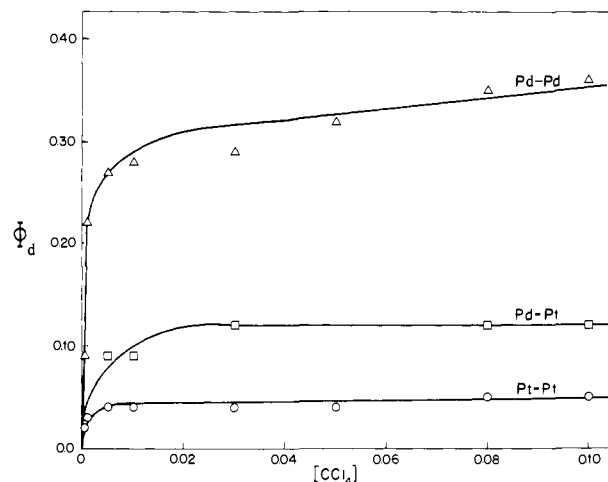
in Figure 5. All quantum yields in Figure 5 were recorded at an average light intensity at 313 nm of $I_a = 1.8 \times 10^{-7}$ einstein/s.

Several key findings emerge from the Φ_d vs. $[CCl_4]$ studies. First, the greater quantum efficiency for the reaction of $Pd_2(CNMe)_6^{2+}$ relative to $PdPt(CNMe)_6^{2+}$ or $Pt_2(CNMe)_6^{2+}$ is maintained over nearly the entire range of CCl_4 concentrations. Within the context of $\sigma \rightarrow \sigma^*$ photochemistry of metal–metal bonds, the lower quantum yields for a third row compared to a second row transition metal complex does have precedent. However, the differences are not generally as great. For example, quantum yields for Cl-atom abstraction by $Cp_2Mo_2(CO)_6$ and $Cp_2W_2(CO)_6$ at 366 nm and comparable light intensities are 0.45 and 0.21, respectively.[11] The higher quantum yields for $Pd_2(CNMe)_6^{2+}$ may be interpreted in terms of two limiting models. On the one hand, an intrinsically higher reactivity of photogenerated $\cdot Pd(CNMe)_3^+$ compared to $\cdot Pt(CNMe)_3^+$ radicals may serve to *increase* the quantum yield for $Pd_2(CNMe)_6^{2+}$. On the other, rapid photochemically nonproductive processes notably radical–radical recombination and excited state nonradiative decay may serve to *decrease* quantum yields to a greater extent for $Pt_2(CNMe)_6^{2+}$. The relative reactivity of photogenerated $\cdot Pt(CNMe)_3^+$ compared to $\cdot Pd(CNMe)_3^+$ radicals is considered in more detail in section D. A second finding from the Φ vs. $[CCl_4]$ studies is that the quantum yields for Cl abstraction by the three $MM'(CNMe)_6^{2+}$ complexes reach limiting values at low $[CCl_4]$. In the case of $Pt_2(CNMe)_6^{2+}$, values of Φ_d show essentially no dependence on $[CCl_4]$ at concentrations above 0.005 M. The independence of Φ_d from $[CCl_4]$ is consistent with a relatively short lifetime for $\cdot Pt(CNMe)_3^+$ radicals in the presence of CCl_4. We note the independence of Φ_d from $[CCl_4]$ is further consistent with a non-chain-radical process, presumably involving direct Cl abstraction by $\cdot Pt(CNMe)_3^+$ radicals. The palladium species does show a slight increase in Φ_d as $[CCl_4]$ approaches 0.1 M, suggesting longer lived $\cdot Pd(CNMe)_3^+$ radicals or a small contribution to the net reaction from a chain mechanism propagated through CCl_4. An alternative mechanism to account for the dependence of Φ_d on $[CCl_4]$ for $Pd_2(CNMe)_6^{2+}$ is association of CCl_4 with ground-state $Pd_2(CNMe)_6^{2+}$ followed by direct dimeric excited-state $\{Pd_2(CNMe)_6^{2+} \cdot CCl_4\}^*$ Cl abstraction. However, the observed halogen atom abstraction photochemistry of the MM'-$(CNMe)_6^{2+}$ complexes appears to be most consistent with photochemical lability of the M–M' bonds.

Excited-state lability of metal–ligand bonds has been invoked to partially account for the photochemistry of $Mn_2(CO)_{10}$, Re_2-$(CO)_{10}$, and related complexes. In the present study, however, we find that the M–CNMe bonds are very labile in the *ground-state complexes*, $MM'(CNMe)_6^{2+}$ (M = M' = Pd, Pt; M = Pd, M' = Pt). The ground-state lability of these complexes is not

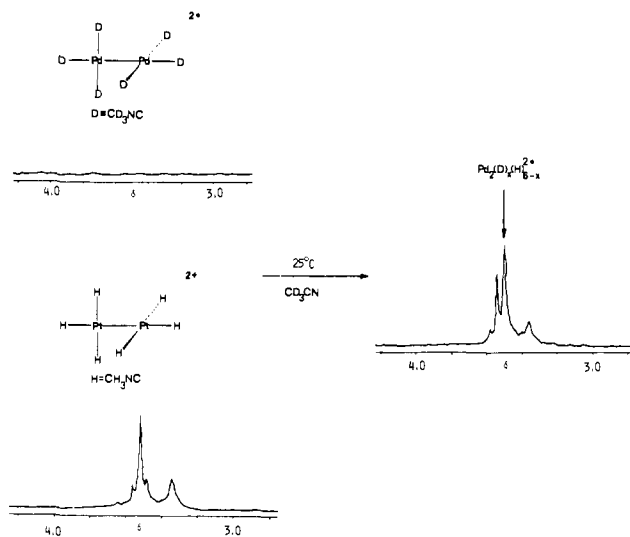**Figure 6.** ^{1}H NMR spectra (200 MHz) for the thermal crossover between metal–ligand bonds of $Pd_2(CNCD_3)_6^{2+}$ and $Pt_2(CNCH_3)_6^{2+}$. The spectra at the left correspond to 0.01 M solutions of $Pd_2(CNCD_3)_6^{2+}$ and $Pt_2(CNCH_3)_6^{2+}$ in acetonitrile-d_3. Upon mixing, a new signal corresponding to the crossover product, $[Pd_2(CNCD_3)_x(CNCH_3)_{6-x}]^{2+}$, is evident at right.

Figure 7. Scheme for competitive Cl-atom abstraction by photogenerated ·$Pd(CNR)_3^+$ and ·$Pt(CNR)_3^+$ radicals. In the limit that radical recombination to form binuclear products is diffusion controlled the relative rate constants for Cl abstraction are related by the following: $k_{Pt}/k_{Pd} = \{[Pt–Cl]/[Pd–Cl]\}\{[Pd–Pd]/[Pt–Pt]\}^{1/2}$.

surprising in view of their 32 valence electron count and attendant coordinative unsaturation. Previous studies of $Pd_2(CNMe)_6^{2+}$, however, did not reveal evidence for lability of Pd–CNMe bonds in acetone solutions, based largely on unsuccessful attempts to trap free CNMe.[40,43] We have therefore carried out metal–ligand crossover experiments in efforts to elucidate the nature of the exchange process which equilibrates the 6 CNMe ligands of $Pd_2(CNMe)_6^{2+}$ at 25 °C. Crossover experiments have involved $Pt_2(CNCH_3)_6^{2+}$ and the totally deuterated palladium analogue, $Pd_2(CNCD_3)_6^{2+}$. The result of mixing $Pt_2(CNCH_3)_6^{2+}$ and $Pd_2(CNCD_3)_6^{2+}$ in acetonitrile-d_3 is given in Figure 6. A new species corresponding to $[Pd_2(CNCD_3)_x(CNCH_3)_{6-x}]^{2+}$ is evident by 200-MHz ^{1}H NMR within the time the first spectrum can be recorded after mixing. The degree of incorporation of CH_3NC into $[Pd_2(CNCD_3)_x(CNCH_3)_{6-x}]^{2+}$ depends only on the mole ratios of $Pd_2(CNCD_3)_6^{2+}$ and $Pt_2(CNCH_3)_6^{2+}$. No further changes in incorporation of $CNCH_3$ can be observed after the first spectrum is recorded. These results suggest the M–CNMe bonds of the $M_2(CNMe)_6^{2+}$ complexes are indeed very labile. They further suggest that the previously noted exchange process evident in the 25 °C ^{1}H NMR spectrum of $Pd_2(CNCH_3)_6^{2+}$ is not unimolecular. In view of the data reported herein, an intermolecular, solvent-assisted, substitution process appears more plausible. The high ground state lability of M–CNMe bonds in this study makes it difficult to assess the relative importance of ligand lability in the excited states. However, it is clear that the ground-state $MM'(CNMe)_6^{2+}$ complexes are completely unreactive toward halogen atom abstraction and M–M' bond homolysis while possessing extremely labile M–CNMe bonds. These observations together with the high excited state reactivity toward M–M' bond homolysis and halogen atom abstraction suggest that it is the homolysis of the metal–metal bonds of these complexes which dominates their photochemistry.

D. Relative Reactivity of Photogenerated ·Pd(CNMe)$_3^+$ and ·Pt(CNMe)$_3^+$ Radicals. As part of our studies, we have examined the role of *radical reactivity* on *quatum efficiency* for the radical process of halogen atom abstraction. It is possible to assess the relative reactivities of photogenerated ·$Pd(CNMe)_3^+$ and ·$Pt(CNMe)_3^+$ radicals by kinetic competition experiments of the general type introduced by Abrahamson and Wrighton.[18] These experiments involve photolysis of the mixed-metal complex, $PdPt(CNMe)_6^{2+}$. The overall kinetic scheme is summarized in Figure 7. Photochemical homolysis of the Pd–Pt bond of $PdPt(CNMe)_6^{2+}$ results in the following pair of radicals: ·$Pd(CNMe)_3^+$ and ·$Pt(CNMe)_3^+$. These radicals may simply re-

combine to reform $PdPt(CNMe)_6^{2+}$, or in the presence of other radicals created during photolysis they may combine to form the homonuclear species $Pd_2(CNMe)_6^{2+}$ or $Pt_2(CNMe)_6^{2+}$. In the presence of CCl_4, the photogenerated radicals may react with CCl_4 to yield either $PdCl(CNMe)_3^+$ or $PtCl(CNMe)_3^+$. It is assumed that ·$Pd(CNMe)_3^+$ and ·$Pt(CNMe)_3^+$ radicals react with CCl_4 in a bimolecular sense with characteristic second-order rate constants k_{Pd} and k_{Pt}. In the limit that the rates of the three different radical recombination processes which form binuclear products are diffusion controlled and comparable, the ratio of rate constants k_{Pt}/k_{Pd} is given by eq 2.[18] It has been determined that

$$k_{Pt}/k_{Pd} =$$
$$\{[PtCl(CNMe)_3^+]/[PdCl(CNMe)_3^+]\}\{[Pd_2(CNMe)_6^{2+}]/$$
$$[Pt_2(CNMe)_6^{2+}]\}^{1/2} \quad (2)$$

photogenerated $CpMo(CO)_3$ and $CpW(CO)_3$ radicals do recombine with essentially diffusion-controlled rate constants $k_r \sim 2$–4 $\times 10^9$ M^{-1} s^{-1}.[10]

In our studies it has been possible to quantitatively determine by 470-MHz ^{1}H NMR the relative reactivity of photogenerated ·$Pd(CNMe)_3^+$ and ·$Pt(CNMe)_3^+$ radicals. This work was facilitated by the fact that each of the species—$Pd_2(CNMe)_6^{2+}$, $PdPt(CNMe)_6^{2+}$, $Pt_2(CNMe)_6^{2+}$, $PdCl(CNMe)_3^+$, and $PtCl(CNMe)_3^+$—can be distinguished by ^{1}H NMR at 470 MHz. Relevant ^{1}H NMR data for the complexes are given in Table II. Figure 8 shows the ^{1}H NMR spectra of a solution initially containing 0.02 M $PdPt(CNMe)_6^{2+}$, 0.4 M CCl_4 in acetonitrile-d_3, during various stages of photolysis. The initial spectrum at the top of the figure indicates $PdPt(CNMe)_6^{2+}$ is the only species in solution. The center spectrum in the figure was recorded after irradiating the sample for 4 min at 313 nm. After 4 min of photolysis, significantly more $PtCl(CNMe)_3^+$ is formed relative to $PdCl(CNMe)_3^+$. Qualitatively, it is clear that photogenerated ·$Pt(CNMe)_3^+$ radicals are more reactive than ·$Pd(CNMe)_3^+$ radicals toward Cl-atom abstraction from CCl_4. The results after 8 min of photolysis show continued formation of predominantly $PtCl(CNMe)_3^+$ and $Pd_2(CNMe)_6^{2+}$. The relative concentrations of each of the photoproducts were obtained by integration of their characteristic peaks in the ^{1}H NMR spectra. Integrations were carried out on difference spectra which were simplified by factored subtraction of the initial spectrum of $PdPt(CNMe)_6^{2+}$. At <50% conversion of $PdPt(CNMe)_6^{2+}$ to photoproducts, the relative reactivity of ·$Pt(CNMe)_3^+$ and ·$Pd(CNMe)_3^+$, k_{Pt}/k_{Pd}, is 4.6 ± 0.2. This value falls off slightly at higher conversions, suggesting

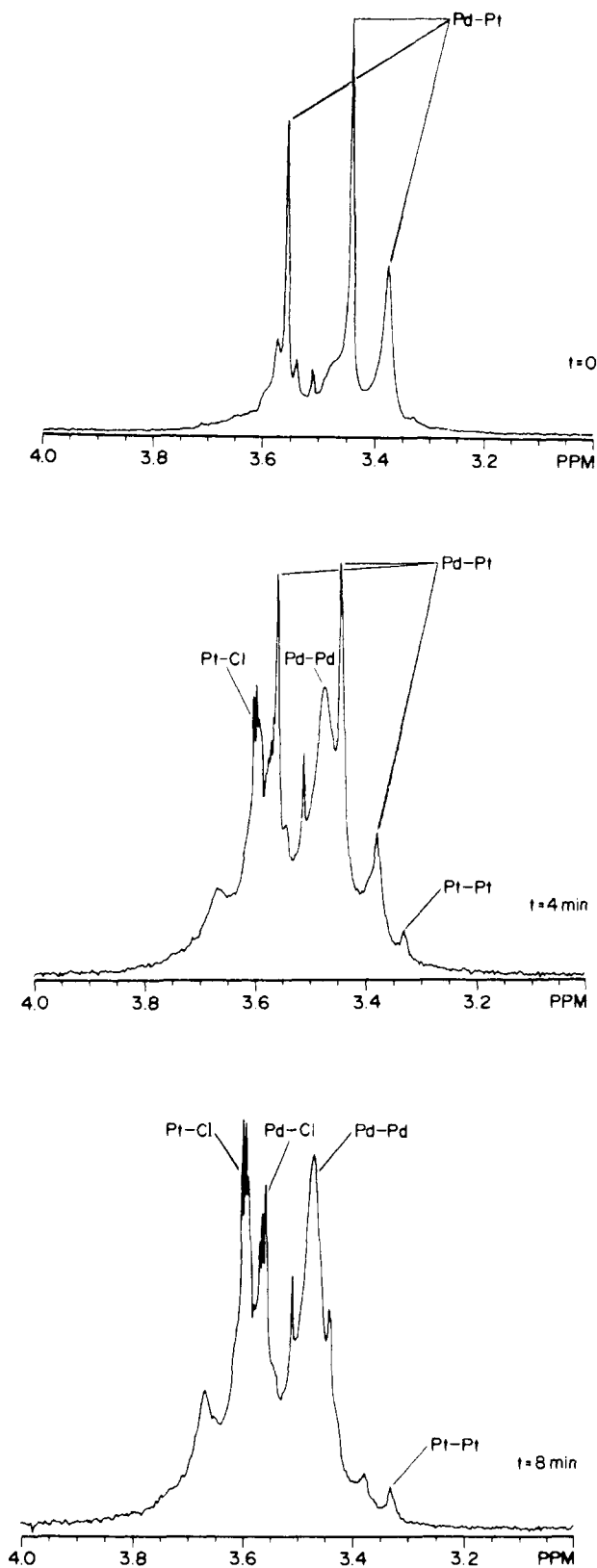Figure 9. Generalized scheme for Cl-atom abstraction photochemistry of $M_2(CNMe)_6^{2+}$ (M = Pd, Pt) complexes.

uncertainty owing to possible differences in the rates of recombination of $\cdot Pd(CNMe)_3^+$ and $\cdot Pt(CNMe)_3^+$. However, Figure 8 does provide unambiguous evidence of significantly greater reactivity of $\cdot Pt(CNMe)_3^+$ compared to $\cdot Pd(CNMe)_3^+$; the trend in relative reactivity is clear.

The *increased reactivity of $\cdot Pt(CNMe)_3^+$* compared to $\cdot Pd(CNMe)_3^+$ is interesting in view of the *decreased quantum yield of $Pt_2(CNMe)_6^{2+}$* toward Cl-atom abstraction. A general scheme for the photochemistry of $M_2(CNMe)_6^{2+}$ (M = Pd, Pt) is presented in Figure 9. Ford and Laine[54] have developed the expression given in eq 3 to estimate the ratio of the square of the Cl-atom

$$\frac{k_m^2}{k_r} = \frac{4I_a}{[CCl_4]^2}\left[\frac{(\Phi_d - \Phi_0)^2}{\Phi_{M-Cl} - (\Phi_d - \Phi_0)}\right] \quad (3)$$

abstraction bimolecular rate constant, k_m, and the radical recombination rate constant, k_r, for $Cp_2W_2(CO)_6$.[54] In eq 3, I_a is the light intensity in einsteins/s, Φ_d and Φ_0 are the disappearance quantum yields of $M_2(CNMe)_6^{2+}$ in the presence and absence of CCl_4, respectively, and Φ_{M-Cl} is the appearance quantum yield of the Cl atom abstraction photoproduct. By employing eq 3 and results of our Φ_d vs. $[CCl_4]$ study (Figure 5), we have estimated $k_m^2/k_r \sim 4 \times 10^{-4}$ M^{-1} s^{-1} for both complexes. This suggests that bimolecular rate constants for Cl-atom abstraction are significantly lower than those for a diffusion-controlled process. If diffusion-controlled recombination, $k_r \sim 2 \times 10^9$ M^{-1} s^{-1}, is assumed, a reasonable estimate of k_{Pd} is $\approx 1 \times 10^3$ M^{-1} s^{-1}, and our relative reactivity studies would put $k_{Pt} \approx 5 \times 10^3$ M^{-1} s^{-1}. Within the context of photogenerated radicals, we find the $\cdot Pd(CNMe)_3^+$ species to be approximately an order of magnitude less reactive than $CpW(CO)_3$,[54] and still less reactive than $\cdot Mn(CO)_5$ and $\cdot Re(CO)_5$[55] toward Cl-atom abstraction. Our relative reactivity studies suggest $\cdot Pt(CNMe)_3^+$ radical reactivity is comparable to that of $CpW(CO)_3$.

Conclusions

The first studies of the photochemistry of σ-bonds between platinum and palladium atoms have been described. The complexes $MM'(CNMe)_6^{2+}$ (M = M' = Pd, Pt; M = Pd, M' = Pt), exhibit intense electronic absorptions at ca. 300 nm which have been assigned to $\sigma \rightarrow \sigma^*$ excitation. Optical excitation into the $\sigma \rightarrow \sigma^*$ absorption bands efficiently leads to the photogeneration of 15-electron $\cdot M(CNMe)_3^+$ radicals. These radicals are reactive toward halogen atom abstraction. The photoproducts of halogen atom abstraction from CX_4 (X = Cl, Br) have been characterized as the mononuclear pesudo-square-planar $MX(CNMe)_3^+$ (M = Pd, Pt; X = Cl, Br) complexes. Quantum yield and relative reactivity studies of Cl abstraction suggest photogenerated $\cdot Pt(CNMe)_3^+$ radicals are significantly more reactive than $\cdot Pd(CNMe)_3^+$. However, quantum efficiencies for Cl abstraction by $Pd_2(CNMe)_6^{2+}$ are also significantly higher than the corresponding Pt complex. Together these observations suggest that radiationless decay (k_{nrd} in Figure 9) depopulates the Pt_2-

Figure 8. ^1H NMR spectra (470 MHz) for competitive Cl-atom abstraction by photogenerated $\cdot Pd(CNR)_3^+$ and $\cdot Pt(CNR)_3^+$ radicals. The initial spectrum corresponds to 0.02 M $[PdPt(CNMe)_6]^{2+}/0.4$ M CCl_4 in acetonitrile-d_3. The center spectrum is of the same solution after 4 min of photolysis at 313 nm and shows significantly more Cl-atom abstraction by $\cdot Pt(CNMe)_3^+$ relative to $\cdot Pd(CNMe)_3^+$. The bottom spectrum was recorded after 8 min of photolysis.

some secondary photolysis. However, the reported value and range of relative bimolecular rate constants for Cl-atom abstraction are obtained reproducibly at low conversions and over several runs. The value of $k_{Pt}/k_{Pd} = 4.6 \pm 0.2$ is of course subject to some
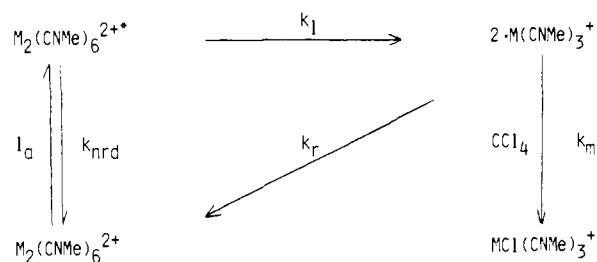
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(CNMe)$_6^{2+}$ excited state more efficiently or that radical escape (k_1) occurs less efficiently than in the case of Pd$_2$(CNMe)$_6^{2+}$. These questions are being explored further in ongoing studies.

Reactions of Re$_2$Cl$_4$(dppm)$_2$ with Carbon Monoxide That Proceed with Retention of the Metal–Metal Bond: Synthesis of Re$_2$Cl$_4$(dppm)$_2$(CO)$_n$ (n = 1, 2) and the Structural Characterization of Cl$_2$Re(μ-Cl)(μ-CO)(μ-dppm)$_2$ReCl(CO)

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Abstract: The triply bonded dirhenium(II) complex Re$_2$Cl$_4$(dppm)$_2$ (dppm = bis(diphenylphosphino)methane) reacts with carbon monoxide to give the carbonyl complexes Re$_2$Cl$_4$(dppm)$_2$(CO)$_n$ (n = 1 or 2). These results provide for the first time evidence as to the nature of the intermediates that are formed in the cleavage of the electron-rich metal–metal triple bond ($\sigma^2\pi^4\delta^2\delta^{*2}$ configuration) by π-acceptor ligands. The neutral complex, Cl$_2$Re(μ-Cl)(μ-CO)(μ-dppm)$_2$ReCl(CO), which has been characterized by X-ray diffraction, crystallizes in the monoclinic system, space group $C2/c$, with a = 22.877 (6) Å, b = 11.044 (3) Å, c = 22.726 (5) Å, β = 123.02 (2)°, V = 4814 (4) Å^3, and Z = 4. The crystal structure was refined to residuals of R = 0.0298, R_w = 0.0285, and quality-of-fit = 1.043. The Re–Re bond distance is 2.584 (1) Å, and the molecule comprises a pair of distorted, edge-sharing octahedra. The bridging and terminal Cl and CO ligand sites are disordered in a well-defined manner. A comparison of the spectroscopic properties (IR, and ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR) of the dicarbonyl complex with those of its ^{13}CO labeled analogue accord with the structure found in the solid state, although ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectroscopy show that there is a fluxional process that renders the carbonyl ligands equivalent between room temperature and ca. –20 °C. The monocarbonyl has been shown by IR spectroscopy to exist as a mixture of two isomers both in the solid state and in solution. The NMR spectral properties of this complex (^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H}) are consistent with an A-frame ↔ non-A-frame fluxionality that keeps the CO ligand bound to a single rhenium atom only.

The reactions of π-acceptor ligands with dimetal complexes that contain metal–metal multiple bonds have been studied extensively.[2-4] It is well-known, for example, that quadruply bonded Mo$_2^{4+}$ [5-7] and Re$_2^{6+}$ [8-11] complexes undergo cleavage reactions with isocyanide ligands and with carbon monoxide to afford stable mononuclear species. Similarly, complexes of the type Re$_2$X$_4$-

(PR$_3$)$_4$ (X = Cl or Br; PR$_3$ = PEt$_3$ or P-n-Pr$_3$) possessing a triple bond and a $\sigma^2\pi^4\delta^2\delta^{*2}$ electronic configuration react with CO to yield the monomeric products ReCl(CO)$_3$(PR$_3$)$_2$ and/or *trans*-ReCl$_2$(CO)$_2$(PR$_3$)$_2$ that are the results of reductive and nonreductive cleavage, respectively.[12] We have also investigated the carbonylation reactions of the series [Re$_2$Cl$_4$(PMe$_2$Ph)$_4$]$^{n+}$ (n = 0, 1, or 2),[13] in which the Re(I) complexes ReCl(CO)$_2$(PMe$_2$Ph)$_3$ and ReCl(CO)$_3$(PMe$_2$Ph)$_2$, as well as the mononuclear Re(III) carbonyl ReCl$_3$(CO)(PMe$_2$Ph)$_3$, are the principle CO-containing products.[11] In none of the aforementioned studies were we able to isolate and identify any reaction intermediate that contained a dinuclear metal–metal bonded unit. However, by resorting to the much more kinetically stable dppm-bridged complex Re$_2$Cl$_4$(dppm)$_2$ (dppm = bis(diphenylphosphino)methane),[14,15] we have recently succeeded

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