Volume 27
Number 21
October 19, 1988

Inorganic Chemistry

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Communications

Photochemistry of $MnRe(CO)_{10}$: Selective Loss of CO from Manganese and Net Substitution To Yield $Mn(CO)_4(PPh_3)Re(CO)_5$

Sir:

We wish to report that near-UV irradiation[1] of $MnRe(CO)_{10}$ in a methylcyclohexane (MCH) glass containing PPh_3 at 77 K yields CO loss, to give $MnRe(CO)_9$ (eq 1), and warming the sample to 298 K results in the formation of $Mn(CO)_4(PPh_3)Re(CO)_5$ (eq 2). Interestingly, thermal reactions of $MnRe(CO)_{10}$

$$MnRe(CO)_{10} \xrightarrow[\text{MCH}]{h\nu,\ 77\text{ K}} MnRe(CO)_9 + CO \qquad (1)$$

$$MnRe(CO)_9 + PPh_3 \xrightarrow[\text{MCH}]{77\text{ K} \rightarrow 298\text{ K}} Mn(CO)_4(PPh_3)Re(CO)_5 \qquad (2)$$

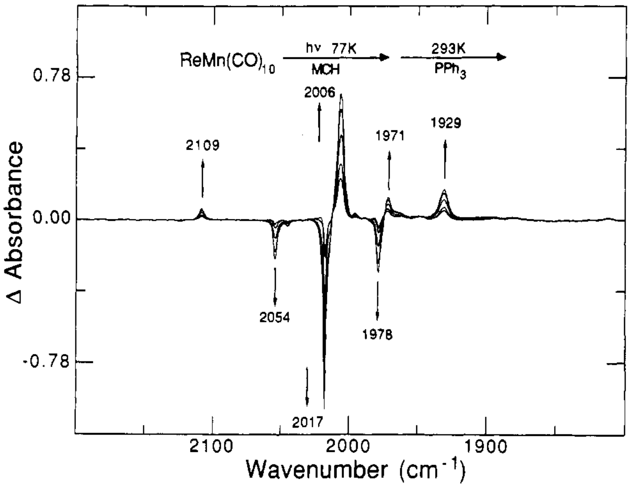

Figure 1. IR difference spectra resulting from successive cycles of irradiation of 3 mM $MnRe(CO)_{10}$ and 30 mM PPh_3 in rigid methylcyclohexane at 77 K followed by warming to room temperature. The product, $Mn(CO)_4(PPh_3)Re(CO)_5$, has absorptions at 2109, 2006, 1971, and 1929 cm^{-1}.

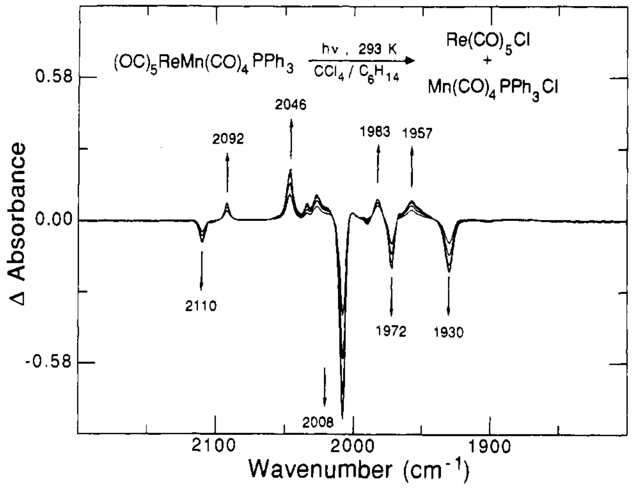

Figure 2. IR difference spectra resulting from 366-nm irradiation of 1 mM $Mn(CO)_4(PPh_3)Re(CO)_5$ in hexane containing 0.1 M CCl_4 at 298 K to yield $Re(CO)_5Cl$ (2046, 1983 cm^{-1}) and $(PPh_3)Mn(CO)_4Cl$ (2092, 2026, 1957 cm^{-1}; 2007 cm^{-1} is obscured by loss of starting material).

with PPh_3 in alkane solutions yield principally the Re-substituted species $Mn(CO)_5Re(CO)_4(PPh_3)$.[2,3] Earlier work has shown that irradiation of $Mn_2(CO)_{10}$,[4,5] $Re_2(CO)_{10}$,[6] and $MnRe(CO)_{10}$[6] leads to loss of CO as the only detectable net photoreaction in a low-temperature rigid medium. In contrast, irradiation of these metal-metal-bonded species in fluid solution at 298 K yields a significant amount of metal-metal bond cleavage and CO loss.[7-11] Heterodinuclear complexes raise the issue of whether photosubstitution occurs selectively at one of the two metal centers, and experiments with $(\eta^5\text{-}C_5R_5)Fe(CO)_2Mn(CO)_5$[12] and $(\eta^5\text{-}C_5H_5)Mo(CO)_3Mn(CO)_5$[13] do show that selective net photosubstitution at the Mn center can be effected. However, in these two cases it was not possible to establish whether the photoejected CO is lost from the Mn center.[12,13] Since $Mn(CO)_5Re(^{13}CO)_5$ is inert with respect to scrambling of the ^{13}CO,[14] it is possible to establish

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(1) Photolysis of the sample in a large Pyrex test tube cooled with liquid N_2 in a Pyrex Dewar flask was carried out by exposing the Dewar flask, rotating on a phonograph turntable, to light from a Hanovia medium-pressure Hg lamp. Similar results are obtained by photolysis in a 1.0 cm path length CaF_2 cell at 93 K, held in a Precision Cell, Inc., Model P/N 21000 variable-temperature cell with CaF_2 windows using liquid N_2 as coolant. A Baush & Lomb SP200 high-pressure Hg lamp filtered by a 10-cm H_2O filter with quartz windows served as a light source.

(2) Sonnenberger, D.; Atwood, J. D. *J. Am. Chem. Soc.* **1980**, *102*, 3484.

(3) Fawcett, J. P.; Pöe, A. J.; Twigg, M. V. *J. Organomet. Chem.* **1973**, *61*, 315.

(4) Wrighton, M. S.; Hepp, A. F. *J. Am. Chem. Soc.* **1983**, *105*, 5934.

(5) Dunkin, I. R.; Härter, P.; Shields, C. J. *J. Am. Chem. Soc.* **1984**, *106*, 7248.

(6) Firth, S.; Hodges, P. M.; Poliakoff, M.; Turner, J. J. *Inorg. Chem.* **1986**, *25*, 4608.

(7) Wrighton, M. S.; Bredesen, D. *J. Organomet. Chem.* **1973**, *50*, C35.

(8) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 2065.

(9) Church, S. P.; Hermann, H.; Grevels, F. W.; Schaffner, K. *J. Chem. Soc., Chem. Commun.* **1984**, 785.

(10) (a) Yasufuku, K.; Hisanao, N.; Iwai, J.-I.; Ohtani, H.; Hoshino, M.; Kobayashi, T. *Organometallics* **1985**, *4*, 2174. (b) Yesaka, H.; Kobayashi, T.; Yasufuku, K.; Nagakure, S. *J. Am. Chem. Soc.* **1983**, *105*, 6249.

(11) Meyer, T. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187.

(12) Pope, K. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 4545.

(13) Pope, K. R.; Wrighton, M. S. *Inorg. Chem.* **1987**, *26*, 2321.

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Table I. Spectroscopic Data for Relevant Compounds

compd	CO region of IR, cm^{-1} (rel OD)[a]	^{31}P NMR data,[b] ppm
PPh_3		−5.1
$[Mn(CO)_4(PPh_3)]_2$[c]	1987 (w), 1963 (s)	75.8 (br)
$[Re(CO)_4(PPh_3)]_2$[c]	1988 (w), 1965 (s)	17.5
$Re_2(CO)_9(PPh_3)$[c]	2107 (0.10), 2034 (0.06), 1998 (1.0), 1968 (0.25), 1941 (0.24)	14.9
$MnRe(CO)_{10}$	2054 (0.20), 2017 (1.0), 1978 (0.28)	
$Mn(CO)_5Re(CO)_4(PPh_3)$	2095 (0.18), 2030 (0.28), 1988 (1.0), 1969 (0.35), 1946 (0.18)	15.1
$MnRe(CO)_8(PPh_3)_2$[c]	1986 (w), 1959 (s), 1909 (w)	77.7 (br); 15.3
$Mn(CO)_4(PPh_3)Re(CO)_5$	2109 (0.09), 2006 (1.0), 1971 (0.20), 1929 (0.23)	75.5 (br)
$Mn(CO)_5Cl$	2056 (1.0), 2000 (0.35)	
$Re(CO)_5Cl$	2046 (1.0), 1983 (0.41)	
$(PPh_3)Mn(CO)_4Cl$	2092 (0.45), 2026 (0.69), 2007 (1.0), 1957 (0.55)	41.3 (br)
$(PPh_3)Re(CO)_4Cl$	2105 (0.24), 2018 (0.71), 2002 (1.0), 1945 (0.56)	4.4

[a] IR data for alkane solutions at 298 K. [b] For toluene or chloroform solutions; chemical shifts are relative to an external standard of 85% phosphoric acid. [c] From ref 3.

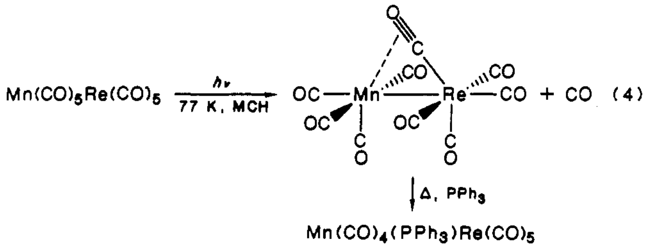
that the Mn center is the source of the photoejected CO.[15] However, it has not been shown that selective photosubstitution of $MnRe(CO)_{10}$ occurs, because the site of N_2 attachment in photogenerated $MnRe(CO)_9(N_2)$ could not be established.[16] Our new results show that coordinatively unsaturated $MnRe(CO)_9$ resulting from CO loss from Mn reacts with PPh_3 to give only the Mn-substituted species $Mn(CO)_4(PPh_3)Re(CO)_5$, despite the fact that $MnRe(CO)_9$ has a semibridging or fully bridging CO.[6]

Figure 1 shows IR spectral changes[17] consistent with the chemistry represented by eq 1 and 2. The initial sample is a 75-mL deoxygenated MCH solution of 3 mM $MnRe(CO)_{10}$ and 30 mM PPh_3. The procedure used to obtain the data shown in Figure 1 involves near-UV irradiation of the sample at 77 K followed by warming to 298 K, withdrawing an aliquot for IR analysis, and returning the sample to 77 K for additional irradiation/warming/analysis cycles. The IR data show net consumption of >50% of the original $MnRe(CO)_{10}$ (bands disappear at 2054, 2017, and 1978 cm^{-1}) and clean formation of $Mn(CO)_4(PPh_3)Re(CO)_5$ (bands appearing at 2109, 2006, 1971, and 1929 cm^{-1}). There is no IR evidence for net generation of $Mn(CO)_5Re(CO)_4(PPh_3)$, which has IR absorptions at 2095, 2030, 1988, 1969, and 1946 cm^{-1} (Table I). The $Mn(CO)_4(PPh_3)Re(CO)_5$ photoproduct can be isolated as a pure material[18] and shows a broad ^{31}P NMR[19] resonance at 75.5 ppm, consistent with Mn-bound, not Re-bound, PPh_3 (Table I). Further proof for the assignment of the photosubstitution product as $Mn(CO)_4(PPh_3)Re(CO)_5$ comes from the photoproducts obtained upon near-UV irradiation of the compound in hexane solution containing 0.1 M CCl_4 (Figure 2). The only primary products found are $Re(CO)_5Cl$ and $Mn(CO)_4(PPh_3)Cl$ (eq 3).

$$Mn(CO)_4(PPh_3)Re(CO)_5 \xrightarrow[\text{hexane/0.1 M } CCl_4]{h\nu} Re(CO)_5Cl + Mn(CO)_4(PPh_3)Cl \quad (3)$$

There is no evidence for $Mn(CO)_5Cl$ or $Re(CO)_4(PPh_3)Cl$, which would be expected if photosubstitution of $MnRe(CO)_{10}$ yielded $Mn(CO)_5Re(CO)_4(PPh_3)$. Our key finding is that thermal reaction of photogenerated $MnRe(CO)_9$ with PPh_3 yields exclusively the Mn-substituted species $Mn(CO)_4(PPh_3)Re(CO)_5$ (eq 2).

Reaction of PPh_3 with photogenerated $MnRe(CO)_9$ to give $Mn(CO)_4(PPh_3)Re(CO)_5$ (eq 2) is consistent with a $MnRe(CO)_9$ structure formed by loss of CO from Mn yielding a species with a semibridged CO (C-bonded to Re) that then reacts selectively at Mn (eq 4). As found in an Ar matrix at 10 K,[15] we find selective photochemical loss of CO from $Mn(CO)_5Re(^{13}CO)_5$ (~80% ^{13}CO-enriched on Re) upon near-UV excitation in a 2-methyltetrahydrofuran glass. Thus, our new results with PPh_3 show that net photosubstitution can occur at the site from which CO is extruded in the primary photoprocess.



Comparison of photosubstitution of $MnRe(CO)_{10}$ via $MnRe(CO)_9$ generated at low temperature and thermal substitution of $MnRe(CO)_{10}$ in alkanes is interesting. Earlier work[2,3] does appear to show that net thermal substitution of CO by PPh_3 yields $Mn(CO)_5Re(CO)_4(PPh_3)$, despite wide agreement[2,20] that Mn is the more thermally labile center. We find that thermal reaction at ~100 °C of 2 mM $MnRe(CO)_{10}$ and 1 mM $Mn(CO)_4(PPh_3)Re(CO)_5$ in deoxygenated alkane solution containing 20 mM PPh_3 results in reaction of both metal complexes but that $Mn(CO)_4(PPh_3)Re(CO)_5$ reacts significantly more rapidly. The initial products from reaction include mainly $Mn(CO)_4(PPh_3)Re(CO)_4(PPh_3)$ and $Mn(CO)_5Re(CO)_4(PPh_3)$. From this chemistry we conclude that $Mn(CO)_4(PPh_3)Re(CO)_5$ cannot accumulate under conditions where $MnRe(CO)_{10}$ reacts thermally with PPh_3 to give $Mn(CO)_5Re(CO)_4(PPh_3)$. Careful monitoring of the thermal reaction of $MnRe(CO)_{10}$ with PPh_3 shows *both* $Mn(CO)_4(PPh_3)Re(CO)_5$ and $Mn(CO)_5Re(CO)_4(PPh_3)$ in the initial stages (~10%) of reaction. The ability to monitor the chemistry by Fourier transform IR greatly aids in the analysis.

When $Mn(CO)_4(PPh_3)Re(CO)_5$ is reacted with CO at ~100 °C in deoxygenated octane, rapid and quantitative conversion to $MnRe(CO)_{10}$ occurs on a time scale where reaction of $MnRe(CO)_{10}$ with PPh_3 is slow. Since sealed container reactions of metal carbonyls often yield some decomposition leading to an excess of CO, it is likely that thermal reaction of $MnRe(CO)_{10}$ with PPh_3 is complicated by this problem. The complication is that $Mn(CO)_4(PPh_3)Re(CO)_5$ is known[3] to react with CO more rapidly than $Mn(CO)_5Re(CO)_4(PPh_3)$. We find, for example, small yields of $MnRe(CO)_{10}$ when $Mn(CO)_4(PPh_3)Re(CO)_5$ is reacted

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(14) Schmidt, S. P.; Basolo, F.; Jensen, C. M.; Trogler, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 1894.

(15) Firth, S.; Hodges, P. M.; Poliakoff, M.; Turner, J. J. *J. Organomet. Chem.* **1987**, *331*, 347.

(16) Firth, S.; Klotzbücher, W. E.; Poliakoff, M.; Turner, J. J. *Inorg. Chem.* **1987**, *26*, 3370.

(17) IR spectra were recorded with either a Nicolet Model 60SX or a 7199 Fourier transform IR spectrometer.

(18) After photolysis, MCH was removed under vacuum, yielding a pale yellow substance, which was passed down a 70–230-mesh alumina column (EM Science), eluted with 1:1 hexane/toluene, and then chromatographed on 1 mm thick silica gel on 20 × 20 cm plates (EM Science) with 2:1 hexane/toluene as eluent. The product, a yellow band with an R_f value of 0.5, was collected by washing the removed silica containing the band with toluene through a Büchner funnel. Solvent was removed under vacuum, yielding a fine yellow powder.

(19) ^{31}P NMR spectra were recorded on a Varian Model XL-300 Fourier transform NMR spectrometer.

(20) (a) Haines, L. I. B.; Hopgood, D.; Pöe, A. J. *J. Chem. Soc. A* **1968**, 421. (b) Haines, L. I. B.; Pöe, A. J. *J. Chem. Soc. A* **1969**, 2826. (c) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3160.

thermally at temperatures where $MnRe(CO)_{10}$ undergoes substitution by PPh_3, showing that some CO release from decomposition occurs. $Mn(CO)_4(PPh_3)Re(CO)_5$ also gives both $Mn(CO)_4(PPh_3)Re(CO)_4(PPh_3)$ and $Mn(CO)_5Re(CO)_4(PPh_3)$ in early stages (~10%) of thermal reaction.

The principal conclusion to be drawn from our work is that the low-temperature photochemical route is the best way to effect clean formation of $Mn(CO)_4(PPh_3)Re(CO)_5$ from $MnRe(CO)_{10}$. We confirm selective loss of CO from Mn upon photoexcitation of $MnRe(CO)_{10}$.[15] Further, thermal activation of $Mn(CO)_4(PPh_3)Re(CO)_5$ yields facile rupture of the Mn–PPh_3 bond to give substitution. We find that $Mn(CO)_4(PPh_3)Re(CO)_5$ cannot survive the conditions where careful analysis of thermal chemistry of $MnRe(CO)_{10}$ (at early stages in the reaction) shows greater lability at Mn, as expected from a variety of other studies.[2,3,20]

Acknowledgment. We thank the National Science Foundation for support of this research.

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Received June 10, 1988

Photoinduced C-S Bond Cleavage by Tetrakis(pyrophosphito)diplatinum(II)

Sir:

The search for inorganic complexes for photochemical multielectron atom transfer reactions is the target of our research. Recent studies have shown that the $Pt_2(P_2O_5H_2)_4^{4-}$ complex (Pt_2) possesses unique photochemistry; for example, it facilitates photochemical H atom abstraction of alcohols and cyclohexene and cleavage of carbon–halogen bonds.[1-3] Its $^3A_{2u}$ state (denoted here $^3Pt_2^*$) is long-lived ($\tau \approx 9.8\ \mu s$), is biradical in character, and is a powerful one-electron reductant.[4] These properties make $^3Pt_2^*$ an ideal system for mechanistic investigation of metal ion induced homolytic C–X bond cleavage reactions, which are sometimes difficult to study by conventional means. We describe here the first example of photochemical cleavage of C–S bonds by transition-metal complexes. Despite the importance of C–S bond cleavage in desulfurization reactions, relatively little is known about the actual mode of the reaction.[5]

The Pt_2 complex does not react with R_2S thermally, although oxidation to $[Pt_2(P_2O_5H_2)_4(SEt_2)_2]^{2-}$ (λ_{max} 342 nm)[6] can be brought about by H_2O_2. In degassed methanol, the phosphorescence but not fluorescence of Pt_2 is quenched by R_2S (R = CH_3, C_2H_5, $(CH_3)_3C$, $PhCH_2$). Values of the quenching rate

Table I. Bimolecular Rate Constants for Quenching of $^3Pt_2^*$ by R_2S in Methanol at 25 °C

substrate	k_q, $M^{-1}\ s^{-1}$	substrate	k_q, $M^{-1}\ s^{-1}$
$(PhCH_2)_2S$	$\sim 10^7$ [a]	$^tBu_2S$	6.3×10^5
Me_2S	9.7×10^5	Et_2S	4.2×10^5

[a] The k_q value is only approximate since the Stern–Volmer plot is not linear. Since the absorption and emission spectra of $Pt_2(P_2O_5H_2)_4^{4-}$ are unaffected by $(PhCH_2)_2S$, there is no ground-state association process that leads to static quenching. However, the quenching rate is found to vary with the laser energy, indicating the possibility of having secondary quenching.

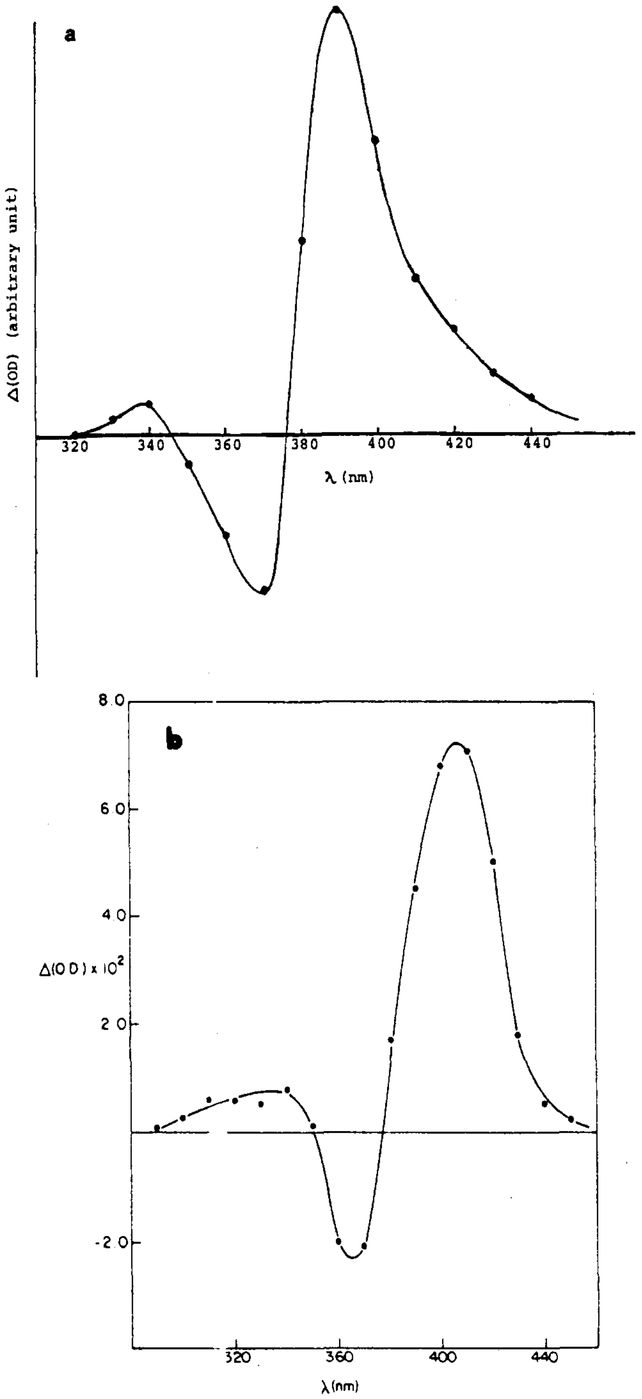

Figure 1. (a) Transient difference absorption spectrum recorded 5 μs after laser flash of a degassed methanolic solution of Pt_2 and Et_2S (~0.1 M). (b) Difference absorption spectrum between $[Pt^{II}Pt^{III}(P_2O_5H_2)_4(SCN)]^{4-}$ and $[Pt_2(P_2O_5H_2)_4]^{4-}$.

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(1) (a) Che, C.-M.; Lee, W.-M. *J. Chem. Soc., Chem. Commun.* **1986**, 512. (b) Che, C-M.; Lee, W.-M.; Cho, K.-C.; Harvey, P. D.; Gray, H. B., submitted for publication in *J. Phys. Chem.* (c) Che, C.-M.; Cho, K.-C.; Chan, W.-S.; Gray, H. B. *Inorg. Chem.* **1986**, *25*, 4906.

(2) (a) Roundhill, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 4354. (b) Roundhill, D. M.; Atherton, S. J.; Shen, Z.-P. *J. Am. Chem. Soc.* **1987**, *109*, 6076. (c) Roundhill, D. M.; Atherton, S. J. *Inorg. Chem.* **1986**, *25*, 4071. (d) Roundhill, D. M.; Shen, Z.-P.; Atherton, S. J. *Inorg. Chem.* **1987**, *26*, 3833.

(3) (a) Marshall, J. L.; Stiegman, A. E.; Gray, H. B. In *Excited States and Reactive Intermediates*; Lever, A. B. P., Ed.; ACS Symposium Series 307; American Chemical Society: Washington, DC, 1986; pp 166–176. (b) Vlcek, A.; Gray, H. B. *J. Am. Chem. Soc.* **1987**, *109*, 286. (c) Vlcek, A.; Gray, H. B. *Inorg. Chem.* **1987**, *26*, 1997. (d) Harvey, P. D.; Gray, H. B. *Nouv. J. Chim.* **1987**, *11*, 595.

(4) (a) Che, C.-M.; Butler, L. G.; Gray, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 7796. (b) Peterson, J. R.; Kalyanasundaram, K. *J. Phys. Chem.* **1985**, *89*, 2486.

(5) See for example: (a) Gutierrez, C. G.; Summerhays, L. R. *J. Org. Chem.* **1984**, *49*, 5206. (b) Chan, M.-C.; Cheng, K. M.; Li, M. K.; Luh, T. Y. *J. Chem. Soc., Chem. Commun.* **1985**, 1610.

(6) The $[Pt_2(P_2O_5H_2)_4(SEt_2)_2]^{2-}$ complex has also been characterized by ^{31}P NMR spectroscopy: δ 25.1, J_1(Pt-P) ≈ 2040 Hz.

0020-1669/88/1327-3691$01.50/0