In summary, [(trimethylsilyl)acetyl]trimethylsilane (**1**) represents a valuable synthon in that it may be elaborated in a stereoselective, stepwise manner into di- and trisubstituted enolates and disubstituted α,β-unsaturated acylsilanes. The latter olefin synthesis provides an alternative to the Wittig olefination with the additional feature that the acylsilane group may be converted into a number of synthetically useful functionalities.[17]

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

Cyclopentadienylbis(ligand)nickel(I): Synthesis and Characterization, Including the X-ray Structure of η^5-Cyclopentadienyl-1,1′-bipyridylnickel(I). Observations on the Mechanism of Substitution of Nickelocene

E. Kent Barefield,* D. A. Krost, D. S. Edwards,
D. G. Van Derveer, R. L. Trytko, and S. P. O'Rear

School of Chemistry, Georgia Institute of Technology
Atlanta, Georgia 30332

Alex N. Williamson

Department of Chemistry
North Carolina A&T State University
Greensboro, North Carolina 27411

Received May 20, 1981
Revised Manuscript Received August 1, 1981

The chemistry of nickel in the formal 1+ oxidation state is very poorly defined at present. Although several complexes have been isolated,[1] many have resulted from fortuitous syntheses and most are poorly characterized with respect to structure and reactivity patterns. Nickel(I) species are potential intermediates in reactions that involve Ni(0) $\rightleftharpoons$ Ni(II) conversions, but few efforts have been made to detect them. Evidence is slowly accumulating that indicates Ni(I) species participate in chemistry that is unrelated to their role in a Ni(0) $\rightleftharpoons$ Ni(II) process. For example, various Ni(I) species are claimed to undergo oxidative–addition (to the 3+ state)[2] and to react with oxygen[3a] (to give an adduct) and olefins.[3b]

This communication is a preliminary report on the synthesis and characterization of Ni(I) complexes of formula $[(C_5H_5)NiL_2]$[4] (L = R_3P, R_2POR, $RP(OR)_2$, $P(OR)_3$; L_2 = diphos,[5] arphos,[5] bpy, *o*-phen) including the X-ray structure of CpNi(bpy). Our results indicate that these species are intimately involved in a number of reactions of cyclopentadienylnickel complexes. Two examples of this type of Ni(I) complex have been reported. Uhlig and Walther first isolated $CpNi[PhP(n\text{-}Bu)_2]_2$ according to reaction 3[6] and later from (2)[7] (Table I). More recently CpNiN(Ph)NNNPh was prepared from Cp_2Ni and PhN_3.[8]

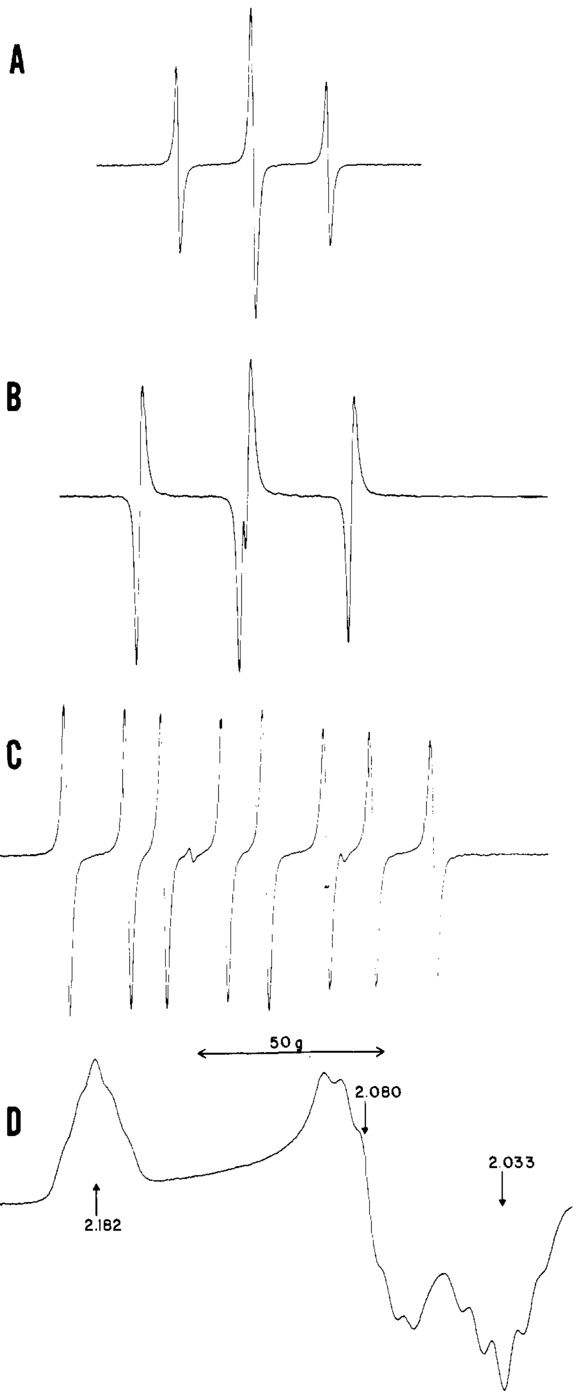


Figure 1. EPR spectra of $CpNiL_2$ Complexes. (A) CpNi(diphos): THF, 25 °C; $g = 2.068$, $A = 122$ G. (B) $CpNi[PPh(OMe)_2]_2$: toluene, 25 °C; $g = 2.052$, $A_1 = 170$ G, $A_2 = 180$ G. (C) CpNi(arphos): THF, 25 °C; $g = 2.075$, $A_P = 100$ G, $A_{As} = 170$ G. (D) CpNi(bpy): THF, −196 °C; $g_1 = 2.184$, $g_2 = 2.080$, $g_3 = 2.033$, $A_1 = 8.4$ G, $A_2 = 8.8$ G, $A_3 = 11.3$ G (from simulated spectrum).

Each of the reactions listed in Table I produced an EPR active product, although when L was a phosphorus(III) ester the EPR signal decayed after a short time regardless of the method of preparation. The same EPR active products were obtained in several cases by electrochemical reduction of $[CpNiL_2]^+$ salts. Sample spectra are shown in Figure 1. Spectra of complexes that contain identical phosphorus ligands consist of 1:2:1 triplets except for the $PhP(OMe)_2$ and $P(OMe)_3$ complexes which give a doublet of doublets.[9,10] Superhyperfine splitting was not resolved in the

---

(1) Nag, K.; Chakravorty, A. *Coord. Chem. Rev.* **1980**, *33*, 87.

(2) (a) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 7547. Smith, G.; Kochi, J. K. *J. Organomet. Chem.* **1980**, *198*, 199 and references cited. (b) Healy, K. P.; Pletcher, D. *J. Organomet. Chem.* **1978**, *161*, 109. Gosden, C.; Healy, K. P.; Pletcher, D. *J. Chem. Soc., Dalton Trans.* **1978**, 972. (c) Tait, A. M.; Hoffman, M. Z.; Hayon, E. *Inorg. Chem.* **1976**, *15*, 934.

(3) (a) Vasilevskis, J.; Olson, D. C.; Loos, K. *Chem. Commun.* **1970**, *1718*. (b) D'Aniello, M. J., Jr.; Barefield, E. K. *J. Am. Chem. Soc.* **1978**, *100*, 1474. Another claim for Ni(I)-olefin chemistry has been discounted: Druliner, J. D.; English, A. D.; Jesson, J. P.; Meakin, P.; Tolman, C. A. *J. Am. Chem. Soc.* **1976**, *98*, 2156.

(4) Hereafter C_5H_5 will be abbreviated as Cp when the group is known or suspected to be bonded in pentahapto fashion.

(5) Diphos is $Ph_2PCH_2CH_2PPh_2$; arphos is $Ph_2AsCH_2CH_2PPh_2$.

(6) Uhlig, E.; Walther, H. *Z. Chem.* **1971**, *11*, 23.

(7) Uhlig, E.; Walther, H. *Z. Anorg. Allg. Chem.* **1974**, *409*, 89.

(8) Overbosch, P.; van Koten, G.; Overbeek, O. *J. Am. Chem. Soc.* **1980**, *102*, 2091.

(9) The reason for the nonequivalence of the two donors in not known.

(10) Mixed ligand complexes result from reaction of $CpNiL_2$ with L′. The following complexes have been identified: $\{CpNi[PhP(n\text{-}Bu)_2][P(OMe)_3]\}$, $g = 2.057$, $A_{P_1} = 189$ G, and $A_{P_2} = 135$ G; $\{CpNi[P(n\text{-}Bu)_3][P(OMe)_3]\}$, $g = 2.055$, $A_{P_1} = 212$ G, and $A_{P_2} = 140$ G; $\{CpNi[PhP(n\text{-}Bu)_2](CO)\}$, $g = 2.036$ and $A_P = 150$ G. For comparison, the parameters of the precursor complexes are as follows: $PhP(n\text{-}Bu)_2$, $g = 2.076$, $A = 117$ G; $P(n\text{-}Bu)_3$, $g = 2.075$, $A = 125$ G; for the bis(trimethyl phosphite) complex, $g = 2.051$ and $A = 193$ and 208 G.

0002-7863/81/1503-6219$01.25/0

Table I. Reactions Leading to Formation of $CpNiL_2$ Complexes

reactants	ligands and conditions[a, b]
(1) $(Ph_3P)_3NiCl + NaCp$	THF, room temperature
(2) $Cp_2Ni + L_4Ni$	L = Ph_3P; THF, 25 °C. L = $PhP(n\text{-}Bu)_2$; THF or hexane, 60 °C. L = diphos, $PhP(CH_3)_2$, Ph_2PCH_3, THF, 60 °C.
(3) $Cp_2Ni + 2L$ or L_2	L = $PhP(n\text{-}Bu)_2$, $P(n\text{-}Bu)_3$, PEt_3, bpy, *o*-phen, diphos; THF or hexane, 60 °C. L = Ph_2POMe, $PhP(OMe)_2$ (1%), $P(OMe)_3$; toluene, 25 °C.
(4) $CpNiL_2^+ + NaCp$	L = diphos (100%), PPh_3, $PhP(n\text{-}Bu)_2$, $P(n\text{-}Bu)_3$ (67%), Ph_2POMe (4%); THF, 25 °C.
(5) $L_2NiX_2 + NaCp$ X = Cl, Br	L = diphos (98%), bpy, arphos, PPh_3, $PhP(n\text{-}Bu)_2$, (92%), PMe_3, $PhPMe_2$, $P(n\text{-}Bu)_3$ (55%); THF; 25 °C.
(6) CpNiNO + excess L	L = $PhPMe_2$, $P(n\text{-}Bu)_3$; hexane or benzene, 50 °C.
(7) $[CpNiCO]_2$ + excess L[d]	L = $PhP(n\text{-}Bu)_2$, $P(n\text{-}Bu)_3$, $P(OMe)_3$; THF, 25 °C.
(8) $[CpNi(CH_2PPh_3)_2]^+ + 2L$	L = $P(OMe)_3$, $P(n\text{-}Bu)_3$; THF, 25 °C.

[a] All reactions were conducted under N_2 in a glove box or with appropriate glassware. EPR samples were prepared in the glove box. [b] Yields are highly variable as are stabilities of the products. Most reactions were not surveyed for yield; the yields indicated were obtained by comparison of the integral of the EPR spectrum taken on a filtered reaction mixture with that obtained for $Ti(acac)_3$ in a THF solution of known and comparable concentration. Since Ni(I) complexes of phosphorus(III) ester are unstable, the value given refers to the highest conversion seen in a given experiment. [c] Phosphines of the type Ph_2PR, as well as Ph_3P, yield $L_4Ni_{(s)}$ in hexane although very weak EPR signals due to the nickel(I) species were detectable for the green supernatant which contained unreacted nickelocene. Reactions conducted in THF were homogeneous, and strong EPR signals due to the Ni(I) complex were observed. [d] EPR signals corresponding to CpNi(CO)L were also detected for L = $P(OMe)_3$.[12] Ultimate products are $Cp_2Ni + Ni(CO)_2L_2$ (Ellgen, P. C. *Inorg. Chem.* 1971, *10*, 232).

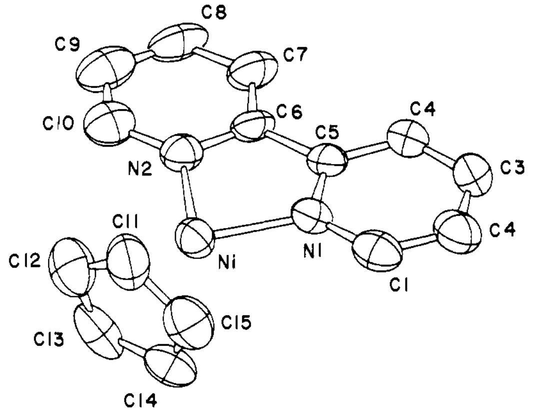


Figure 2. ORTEP drawing of CpNi(bpy). Hydrogen atoms are not shown; probability ellipsoids are shown at the 50% level. Numbering scheme applies to data in Tables 4–7 in the supplementary material.

isotropic spectra of the bpy and *o*-phen derivatives; however, the expected five-line patterns were observed for each g tensor component of anisotropic spectra (illustrated for the bpy complex in Figure 1D).[11] The hyperfine coupling patterns and g values are consistent with the presence of an $S = {}^1/_2$ complex ligated by two group 5 donors.

Although readily formed, the air-sensitive paramagnetic products were very difficult to isolate because of their high solubility and their tendency to decompose to Cp_2Ni and NiL_4, vide infra. However, CpNi(diphos) and CpNi(bpy) (Figure 2) as well as the previously reported $CpNi[PPh(n\text{-}Bu)_2]_2$ were isolated in analytically pure form.[12] Each of these dark-blue compounds has a magnetic moment[13] consistent with their formulation as d^9 complexes, and each had an isotropic EPR spectrum identical with that observed for the appropriate reaction mixtures listed in Table I. These observations strongly suggest that all of the EPR active products have the composition $CpNiL_2$ and contain nickel in the formal 1+ oxidation state.

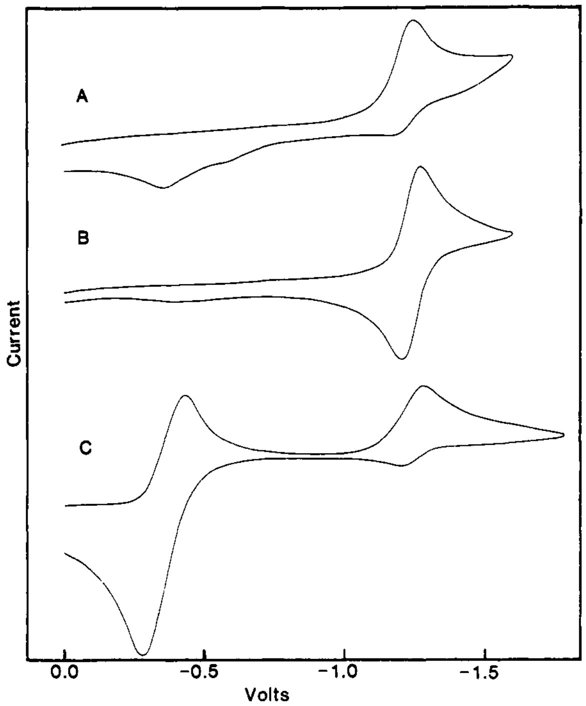


Figure 3. Cyclic voltammetry traces obtained at 200 mV/s on 0.1 M $(n\text{-}Bu)_4NBF_4/CH_3CN$ solutions vs. 0.1 M Ag^+/Ag reference. (A) 10^{-3} M $[CpNi(PPh_3)_2]PF_6$; (B) 10^{-3} M $[CpNi(PPh_3)_2]PF_6$ + 10^{-2} M PPh_3; (C) 10^{-3} M Cp_2Ni + 10^{-3} M $Ni(PPh_3)_4$.

Unfortunately, the EPR data provide no details concerning the mode of bonding of the cyclopentadienyl group to the nickel atom. By conventional electron counting, the complexes are 19 or 17 e^- systems depending upon whether the C_5H_5 moiety is bonded in η^5 or η^3 fashion. Uhlig and Walther tentatively suggested,[7] on the basis of infrared spectral data, that the cyclopentadienyl group in the $PhP(n\text{-}Bu)_2$ complex might be bonded in an η^3 manner. An X-ray structure determination[14] on the bpy complex

---

[11] $\overline{CpNiN(Ph)NNNPh}$[8] also displays a rhombic EPR spectrum at -196 °C (THF–toluene) $g_1 = 1.97$, $g_2 = 2.01$, and $g_3 = 2.08$. Only g_2 shows superhyperfine splitting by the two nitrogen donors.

[12] The bpy complex was prepared by reaction 3 (Table I); 3–5-h reflux followed by filtration and subsequent evaporation of the THF solvent. Bpy/Ni ratios up to 3:1 were employed. The yield of dark blue-violet product was about 40%. The crystal of this complex chosen for X-ray analysis was obtained by evaporative cooling of a THF solution. The diphos complex was prepared by reaction 5. After a 2 h reaction time the THF solution was evaporated and the residue taken up in benzene and passed over a short alumina column. Concentration of the solution gave a blue amorphous solid (78%). The $PhP(n\text{-}Bu)_2$ complex was prepared by Uhlig's procedure[6] in isolated yields in the range 30–60%.

[13] The presence of one unpaired electron is indicated by the magnetic moments (μ_B) of the bpy and diphos complexes which were 1.69 and 1.76, respectively (obtained by the Evans NMR method). Uhlig and Walther found $\mu_B = 1.76$ for the $PhP(n\text{-}Bu)_2$ complex.

[14] Crystal data and details of data collection and refinement details are contained in Tables 2 and 3 (available as supplementary material). The structure was solved by Patterson, difference Fourier, and full-matrix least-squares techniques using the SHELX-76 program package and a CDC Cyber 76/6400 computer. Positional and anisotropic thermal parameters of nonhydrogen atoms were refined. Hydrogen atoms were included in calculated positions (carbon atoms sp^2 hybridization; C–H distances (1.08 Å) with refinement of isotropic thermal parameters. At convergence $R = 0.047$ with $R_w = 0.048$ for 1673 data with $F > 3\sigma(F)$. Data were not corrected for absorption. Tables 4–8 (available as supplementary material) contain final positional and anisotropic thermal parameters for nonhydrogen atoms (Table 4), final positional and isotropic thermal parameters for hydrogen atoms (Table 5), interatomic distances and angles (Table 6), least-squares planes (Table 7) and structure factor tables (Table 8).

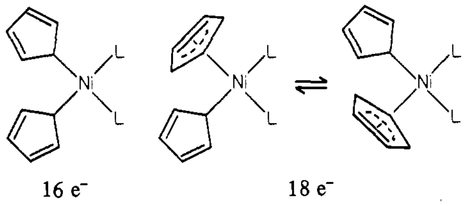
shows that the C_5H_5 group is pentahapto. A drawing of the molecule is shown in Figure 3. Nickel–nitrogen atom distances are equal [1.955 (3) and 1.958 (4)Å], and the cyclopentadienyl ligand is planar[15] with nickel–carbon distances ranging from 2.17 (4) to 2.22 (4) Å.[16] The nickel atom is 1.844 Å from the plane of the cyclopentadienyl carbon atoms which is at an angle of 89.1° to the plane defined by the nickel and bipyridyl ligand atoms. There is no indication of an η^3 interaction for the cyclopentadienyl group of the type found for one ring in $(C_5H_5)_2W(CO)_2$,[17] and CpNi(bpy) should be considered as a 19 e^- species, at least in the solid state.

The reaction of nickelocene with phosphorus ligands is a useful synthetic procedure for preparing NiL_4 complexes. Our results indicate that $CpNiL_2$ complexes are intermediates in these reactions. The stability of the nickel(I) complexes varies considerably; EPR signals for phosphine and nitrogen donor complexes persisted without change in intensity for long periods of time once equilibrium was established, whereas the complexes of phosphorus(III) esters were transients with NiL_4 complexes as the ultimate products. A kinetic study by Werner et al.[18] established the rate law $-d[Cp_2Ni]/dt = k[Cp_2Ni][L]^2$ for the production of $Ni[P(OEt)_3]_4$ in dioxane. It was assumed that the intermediate (clearly $CpNiL_2$) reacted with additional ligand to produce NiL_4 and a second C_5H_5 radical.[19] Although this pathway cannot be excluded, several observations indicate that an alternative pathway involves cyclopentadienyl transfer between two $CpNiL_2$ molecules to yield Cp_2Ni and NiL_4.

The existence of a ring-transfer process is particularly evident for $[CpNi(PPh_3)_2]$. A mixture of Cp_2Ni and $Ni(PPh_3)_4$ (1:1) gave a dark brown solution[20] identical with that obtained from the reaction of $(Ph_3P)_3NiCl$ with NaCp, (both in THF) and an identical 1:2:1 triplet in the EPR spectrum. Cyclic voltammetry scans on $[CpNi(PPh_3)_2]PF_6$ showed a cathodic wave at −1.25 V, a much smaller anodic wave at −1.18 V ($i_p^a/i_p^c < 0.6$), and an anodic wave at −0.35 V corresponding to nickelocene (Figure 3a). CV scans of a mixture of nickelocene and $Ni(PPh_3)_4$ showed the same irreversible process observed for the cationic complex (Figure 3c).[21] Thus nickelocene and the Ni(0) complex are in equilibrium with the Ni(I) complex and the disproportionation of Ni(I) is fast compared to the CV time scale. Addition of a 10-fold excess of triphenylphosphine to $[CpNi(PPh_3)_2]^+$ results in completely reversible electrochemical behavior (Figure 3b) and suggests that the formation of nickelocene proceeds via the 17 e^- species, $CpNiPPh_3$, which is formed by dissociation of triphenylphosphine.

Other $CpNiL_2^+$ salts undergo reduction when the potential range is from −1.1 to −1.7 V with varying degrees of reversibility. Anodic waves for one or more products were observed for irreversible cases. In some instances these included nickelocene, but in others it was not detectable.[22] Although both the Ph_2POMe and the $PhP(OMe)_2$ complexes showed reversible behavior, bulk electrolysis produced nickelocene and NiL_4.

Information concerning the mechanism of reduction of $[CpNiL_2]^+$ salts with NaCp (reactions 4 and 5) comes from the following experiment: $CpNi(diphos)^+$ was treated with 1.1 equiv of $C_5D_5^-$ (87% deuterated) in THF, and the resulting Ni(I) product was oxidized with I_2 to give $CpNi(diphos)^+$ in which the cyclopentadienyl ligand was 41% deuterated (determined by integration of the NMR spectrum). This result is consistent with the presence of an intermediate in which the two cyclopentadienyl ligands are bonded to the nickel atom and equilibrated through symmetry or a dynamic process, e.g.,

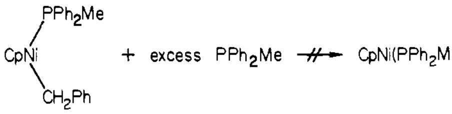


It is not unreasonable to expect that the formation of $CpNiL_2$ from nickelocene occurs via the same type of intermediate.

The ylide complex, $[CpNi(CH_2PPh_3)_2]^+$, which was recently reported as the product of $Cp_2Ni + 2\ CH_2^-PPh_3^+$,[23] is one of the few examples of a product resulting from displacement of $C_5H_5^-$ by a neutral ligand.[24,25] Although only the PF_6^- and BPh_4^- salts were characterized by Booth,[23] we have isolated the cyclopentadienyl salt as the direct product of the displacement reaction and find that it reacts with phosphines to produce $CpNiL_2$ species. No EPR signal was observed for a monophosphine product, which suggests that reduction by the $C_5H_5^-$ anion does not occur until both ylide ligands are substituted. Cyclic voltammetry scans on $[CpNi(CH_2PPh_3)_2]PF_6$ (same conditions as given for Figure 3) showed that the complex was irreversibly reduced at ~−2.2 V but was reversibly *oxidized* with $E_{1/2} = -0.21$ V.

The diverse behavior of the nickelocene $CH_2^-PPh_3^+$ system compared to that of group 5 donors is consistent with the idea that π-bonding ligands stabilize lower oxidation states whereas they are destabilized by coordination of good σ donors. In fact, it is surprising to us that the cyclopentadienide anion functions as a reducing agent in any case if the primary oxidation product is C_5H_5 radical since ΔH_f for the radical is 42 kcal/mol greater than that of the anion (in the gas phase). Anions such as $C_6H_5CH_2^-$ and CH_3^- do not function as reducing agents under similar conditions, e.g.,

$$CpNi(diphos)^+ + CH_3MgBr \not\longrightarrow CpNi(diphos)$$



$$CpNi(PPh_2Me)(CH_2Ph) + \text{excess } PPh_2Me \not\longrightarrow CpNi(PPh_2Me)_2$$

It is not clear whether the nickel–σ-cyclopentadienyl bond is much lower in energy than other nickel–carbon σ bonds or if the effectiveness of the anion as a reducing agent is due to an anchimeric process involving the cyclopentadienyl double bonds.[26] This point as well as other reactions of these fascinating compounds are under study.

Acknowledgment. The combined support of the National Science Foundation and Research Corporation, which supplied funds for purchase of an inert atmosphere box in the early stages

---

[15] Maximum deviation from the least-squares plane defined by the five carbon atoms is 0.006 Å.

[16] For comparison, Cp_2Ni has a Ni–C distance of 2.196 (8) Å (Hedberg, L.; Hedberg, K. *J. Chem. Phys.* **1970**, *53*, 1228) and the Ni–C(Cp) distances average 2.14 Å in $CpNi(PPh_3)Ar$ (Ar = C_6H_5 or C_6F_5) (Churchill, M. R.; O'Brien, T. A. *J. Chem. Soc. A* **1969**, 266; **1968**, 2970).

[17] W–C distances for the η^3 ring were 2.28, 2.40, and 2.98 Å. Huttner, G.; Brintzinger, H. H.; Bell, L. G.; Friedrich, P.; Bejenke, V., Neugebauer, D. *J. Organomet. Chem.* **1978**, *145*, 329.

[18] Werner, H.; Harder, V.; Deckelmann, E. *Helv. Chim. Acta* **1969**, *52*, 1081.

[19] Direct evidence for the formation of C_5H_5 radical has not been obtained.

[20] The blue-violet color observed for other phosphine derivatives is apparently masked by the intense color of $Ni(PPh_3)_4$.

[21] $Ni(PPh_3)_n$ should also be electroactive in this potential range; Kochi reports $E_{1/2}$ for $Ni(PPh_3)_4$ (10^{-3} M in CH_3CN) to be −1.1 V (corrected to 0.1 M Ag/Ag) (Tsou, T. T.; Kochi, J. K.; *J. Am. Chem. Soc.* **1979**, *101*, 6319). However, we have observed poorly defined waves and low diffusion currents for this complex at concentrations $<10^{-3}$ M.

[22] There are a number of possibilities for "decomposition" products including the formation of analogues to the di-μ-(cyclopentadienyl)bis(ligand)dipalladium(I) complexes reported by Werner (Werner, H.; Kraus, H. *J. Chem. Soc., Chem. Commun.* **1979**, 814) and Suzuki (Suzuki, K.; Jindo, A. *Inorg. Chim. Acta* **1980**, *44*, L37). CV studies on $[CpNiL_2]^+$ in the presence of added L have not been made for ligands other than PPh_3.

[23] Booth, B. L.; Smith, K. G. *J. Organomet. Chem.* **1979**, *178*, 361.

[24] The only other example known to us is the claim that Cp_2Ni yields $[Ni(NH_3)_6](C_5H_5)_2$ in NH_3(l). Behrens, J.; Meyer, K. *Z. Naturforsch. B* **1966**, *21B*, 489.

[25] $C_5H_5^-$ is displaced by other anions such as $C_3H_5^-$ (to give $CpNi(\eta^3\text{-}C_3H_5)$: McClellan, W. R.; Hoehn, H. H.; Cripps, H. N.; Muetterties, E. L.; Howk, B. W. *J. Am. Chem. Soc.* **1961**, *83*, 1601) and $Li_2C_8H_6$ [to give bis(pentalenyl)dinickel]: Katz, T. J.; Acton, N. *J. Am. Chem. Soc.* **1972**, *94*, 3281].

[26] Labinger has reported reactions of $CpFe(CO)_2(\eta^1\text{-}C_5H_5)$ with phosphorus ligands that do not occur with other alkyl analogues. Labinger, J. A. *J. Organomet. Chem.* **1977**, *136*, C31. Fabian, B. D.; Labinger, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 2239.

of this work, is gratefully acknowledged. E.K.B. appreciates many helpful and stimulating discussions with Professors E. M. Burgess and C. L. Liotta.

Supplementary Material Available: Tables of crystal data, data collection and refinement details, final positional and anisotropic thermal parameters for nonhydrogen atoms, final positional and isotropic thermal parameters for hydrogen atoms, interatomic distances and angles, least-squares planes, and structure factors (12 pages). Ordering information is given on any current masthead page.

Photolysis of Bis(triphenylphosphine)dioxygenplatinum. Generation of Singlet Oxygen

Arnd Vogler* and Horst Kunkely

Institut für Anorganische Chemie
D-8400 Regensburg, Federal Republic of Germany

Received April 27, 1981
Revised Manuscript Received July 27, 1981

The majority of thermal reactions of coordination compounds proceeds adiabatically.[1] Only a few nonadiabatic reactions, which may be accompanied by chemiluminescence,[3] have been investigated. On the contrary, all photochemical reactions of transition-metal complexes which are known so far are nonadiabatic since the products seem to be formed in electronic ground states.[4] We report here our observation that the photolysis of $[P(C_6H_5)_3]_2PtO_2$, leading to the release of electronically excited singlet oxygen, is an adiabatic reaction.

While certain organic peroxides are well-known to release singlet oxygen photochemically,[2b,7] the photolyses of some peroxo or dioxygen complexes of transition metals such as $[(NH_3)_4Co(\mu\text{-}O_2)(\mu\text{-}NH_2)Co(NH_3)_4]^{4+}$[8] and $[Ir(diphos)_2O_2]^{+}$[9] also lead to the formation of O_2 but apparently in its triplet ground state.

$[P(C_6H_5)_3]PtO_2$[10] dissolved in organic solvents such as $CHCl_3$ starts to absorb at about 450 nm. The extinction increases toward shorter wavelengths (at 300 nm, ϵ 530). A maximum does not appear until a wavelength of 280 nm where the solvent starts to absorb. When these solutions ($\sim 10^{-3}$ M) saturated with O_2 were irradiated ($\lambda_{irr} > 300$ nm), the complex seemed to be almost stable. When the solutions were deaerated with N_2, light absorption caused a slow decomposition, indicated by a small increase of the optical density between 450 and 300 nm. It was assumed that $[P(C_6H_5)_3]_2PtO_2$ photolyzed to $Pt[P(C_6H_5)_3]_2$ and O_2 in the primary photochemical step. In the presence of excess O_2 the starting complex will be regenerated. In the absence of additional O_2 this recombination seems to be accompanied by an unidentified side reaction, possibly an oxidative addition of the solvent.[11] The formation of $Pt[P(C_6H_5)_3]_2$ as the primary photoproduct was confirmed by low-temperature photolysis. At 77 K the photolysis led to the appearance of a blue emission ($\lambda_{max} = 445$ nm) which clearly indicated the generation of $Pt[P(C_6H_5)_3]_2$.[12] The emission intensity increased with irradiation time.

Finally, it was of significance to see whether the photoreleased O_2 was formed in its triplet ground state or an excited singlet state. For the detection of $^1O_2$ we selected 2,2,6,6-tetramethylpiperidine (TMP). It scavenges $^1O_2$ with the formation of a stable nitroxide radical which is easily detectable by ESR spectroscopy at room temperature.[13] The particular advantage of TMP which can be utilized for application in photoreactions is that it does not absorb light at wavelengths longer than 280 nm. In addition, it was shown that the efficiency of $^1O_2$ quenching by TMP derivatives is not very high ($k_q \sim 10^5$ M^{-1} s^{-1}).[13e,14,15] Consequently, the addition of a nonreactive quencher for $^1O_2$ such as the widely used Dabco[14] (1,4-diazabicyclo[2.2.2]octane) with $k_q \sim 2.4 \times 10^7$ M^{-1} s^{-1} should effectively suppress the formation of the nitroxide radical. Such a competition experiment should serve as a further proof for the formation of $^1O_2$.

Upon addition of TMP (2×10^{-3} M) to a solution of $[P(C_6H_5)_3]_2PtO_2$ (2×10^{-3} M) in $CHCl_3$ saturated with N_2, the absorption spectrum of the complex did not change, indicating the absence of a thermal reaction. Upon irradiation (light source: Osram 100 W/2 high-pressure mercury arc; cut-off filter: 310 nm) the extinction of the solution increased between 500 and 300 nm. Simultaneously a strong ESR signal ($g = 2.0059$, hyperfine coupling 16.15 G) developed which is characteristic for the nitroxide radical of TMP formed by the reaction of TMP with $^1O_2$.[13] This experiment was repeated with Dabco (3×10^{-3}M) added to the solution.[16] The ESR signal now was very weak since Dabco apparently intercepted $^1O_2$.

The formation of $^1O_2$ was confirmed by an additional independent test with 1.3-diphenylisobenzofurane (DIF) as a trap for $^1O_2$[17] DIF scavenges $^1O_2$ with high efficiency ($k_1 = 8 \times 10^8$ M^{-1} s^{-1}). Since DIF is somewhat light sensitive,[7,17] careful control experiments had to be carried out. $[P(C_6H_5)_3]_2PtO_2$ ($\sim 10^{-3}$ M) was irradiated ($\lambda_{irr} = 313$ nm) in the presence of DIF ($\sim 4.5 \times 10^{-5}$ M) in a deaerated solution of $CHCl_3$. More than 70% of the incident light was absorbed by the platinum complex. The photolysis was accompanied by a rapid decrease of the absorption maximum at 420 nm, indicating the disappearance of DIF. When DIF was irradiated under identical conditions in aerated or deaerated solutions of $CHCl_3$ in the absence of the complex, only a very slow decrease of the absorption maximum at 420 nm was observed.

In dioxygen complexes of transitions metals electron density is generally shifted from the metal to the dioxygen ligand.[19] This was confirmed by calculations for $(PH_3)_2PtO_2$ which was used as a model for $[P(C_6H_5)_3]_2$ PtO_2.[20] Since the photolysis was accomplished by light absorption into the long-wavelength ab-

---

(1) For definition and classification of adiabatic and nonadiabatic (diabatic) reactions, see ref 2.

(2) (a) Förster, Th. *Pure Appl. Chem.* **1970**, *24*, 443. (b) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, CA, 1978; Chapter 14.

(3) (a) Lyttle, F. E.; Hercules, D. M. *Photochem. Photobiol.* **1971**, *13*, 123. (b) Gafney H. D.; Adamson, A. W. *J. Chem. Educ.* **1975**, *52*, 480. (c) Bolletta, F.; Rossi, A.; Balzani, V. *Inorg. Chim. Acta* **1981** *53*, L23. (d) Vogler, A.; El-Sayed, L.; Jones, R. G.; Namnath, J.; Adamson, A. W. *Inorg. Chim. Acta* **1981**, *53*, L35.

(4) Excited-state protolysis[5] and exciplex formation[6] of transition-metal complexes are adiabatic photoreactions. However, these reactions do not involve substantial nuclear reorganizations and are completely reversible.

(5) (a) Giordano, P. J.; Bock, C. R.; Wrighton, M. S.; Interrante, L. V.; Williams, R. F. X. *J. Am. Chem. Soc.* **1977**, *99*, 3187. (b) Giordano, P. J.; Bock, C. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 6960.

(6) Vogler, A.; Kunkely, H. *Inorg. Chem. Acta* **1980**, 45, L265.

(7) Schmidt, R.; Drews, W.; Brauer, H.-D. *J. Am. Chem. Soc.* **1980**, *102*, 2791.

(8) Valentine, J. S.; Valentine, D. *J. Am. Chem. Soc.* **1971**, *93*, 1111.

(9) Geoffroy, G. L.; Hammond, G. S.; Gray, H. B. *J. Am. Chem. Soc.* **1975**, *97*, 3933.

(10) (a) Tokahashi, S.; Sonogashira, K.; Hagihara, N. *J. Chem. Soc. Jpn.* **1966**, *87*, 610. (b) Wilke, G.; Schott, H.; Heimbach, P. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 92. (c) Nyman, C. J.; Wymore, C. E.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 561.

(11) Sostero, S.; Traverso, O.; Lenarda, M.; Graziani, M. *J. Organomet. Chem.* **1977**, *134*, 259.

(12) Vogler, A.; Wright, R. E.; Kunkely, H. *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 717.

(13) (a) Lion, Y.; Delmelle, M.; Van de Vorst, A. *Nature* (*London*) **1976**, *263*, 442. (b) Cannistraro, S.; Van de Vorst, A. *Biochem. Biophys. Res. Commun.* **1977**, *74*, 1177. (c) Cannistraro, S.; Jori, G.; Van de Vorst; A. *Photochem. Photobiol.* **1978**, *28*, 257. (d) Maillard, P.; Krausz, P.; Giannotti, C.; Gaspard, S. *J. Organomet. Chem.* **1980**, *197*, 285. (e) Ivanov, V. B.; Shlyapintokh, V. Y.; Khvostach, O. M.; Shapiro, A. B.; Rozantsev, E. G. *J. Photochem.* **1975**, *4*, 313.

(14) Bellus, D. "Singlet Oxygen"; Ranby, B., Rabeck, J. F., Eds.; Wiley: New York, 1978; Chapter 9.

(15) Bellus, D.; Lind, H.; Wyatt, J. F. *J. Chem. Soc., Chem. Commun.* **1972**, 1199.

(16) Dabco does not absorb above 300 nm; see ref 14.

(17) Bell, J. A.; MacGillivray, J. D. *J. Chem. Educ.* **1974**, *51*, 677.

(18) Merkel, P. B.; Kearns, D. R. *J. Am. Chem. Soc.* **1975**, *97*, 462.

(19) Vaska, L. *Acc. Chem. Res.* **1976**, *9*, 175.

(20) Norman, J. G. *J. Am. Chem. Soc.* **1974**, *96*, 3327.

0002-7863/81/1503-6222$01.25/0