plitudes, $|F_o|^2$, by means of standard Lorentz and polarization corrections. A correction was also made for the effects of anomalous dispersion associated with the platinum atoms.[15]

The coordinates of the platinum atoms were determined by using heavy-atom Patterson techniques on the 1935 reflections having $I > 3\sigma(I)$ obtained from the 2θ range 3.0–43.0°. The remaining 22 carbon and two oxygen atoms were subsequently located from difference maps (Table IV). The hydrogen atoms were not located. All the atoms were refined with anisotropic thermal parameters, and correction was made for isotropic extinction. During the final cycles of refinement, 3452 reflections having $I > 3\sigma(I)$ obtained from the 2θ range 3.0–55.0° were employed.

The top four peaks in the final difference Fourier (1.66–1.36 e/Å^3) were within 0.86 Å of the Pt atoms. There were no other peaks in the final difference Fourier above the noise level (1.00 e/Å^3).

All calculations were performed on a Data General Eclipse S-200 computer with 64K of 16-bit words, a parallel floating-point processor for 32- and 64-bit arithmetic and a Data General disk with 10-million 16-bit words using versions of the Nicolet (Syntex) E-XTL or SHELXTL interaction crystallographic software package as modified at the Crystalytics Co.

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Registry No. 1, 113792-89-5; 3, 113779-30-9; $[Pt_2Cl_4(CO)_2][NBu_4]_2$, 89554-12-1; $C_5Me_5MgCl\cdot THF$, 107495-40-9; $[PtCl_3(CO)][NBu_4]$, 34964-16-4; $Pt_2(\eta^5\text{-}C_5H_5)_2(CO)_2$, 76680-94-9.

Supplementary Material Available: Tables of crystal data, atomic coordinates, anisotropic thermal parameters, bond lengths, bond angles, and torsion angles (16 pages). A listing of structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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Communications

Photochemical Formation of a Metal–Metal Bond Following Outer-Sphere Intervalence Excitation in the Ion Pair $[Co^{I}(CO)_3(PPh_3)_2][Co^{-I}(CO)_4]$

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Summary: The absorption spectrum of the ion pair $[Co^{I}(CO)_3(PPh_3)_2][Co^{-I}(CO)_4]$ in acetone displays a long-wavelength band at λ_{max} = 386 nm that is assigned to an intervalence transfer (IT) transition from Co^{-I} to Co^{+I}. Upon IT excitation a photoreaction occurs according to the equation $[Co^{I}(CO)_3(PPh_3)_2][Co^{-I}(CO)_4] \rightarrow [(PPh_3)(CO)_3Co^0\text{–}Co^0(CO)_3PPh_3]$ + CO with a quantum yield of Φ = 0.012. It is suggested that in the primary photochemical step the radicals $[Co(CO)_3(PPh_3)_2]$ and $[Co(CO)_4]$ are generated. These radicals are labile and undergo dissociation and substitution reactions and finally dimerize to yield the stable photoproduct.

An important photoreaction of dimeric carbonyl complexes is the homolytic splitting of the metal–metal bonds.[1] McCullen and Brown[2] and then Tyler and co-workers have shown that in the presence of suitable ligands (L) this primary photochemical step is followed by a disproportionation:[3]

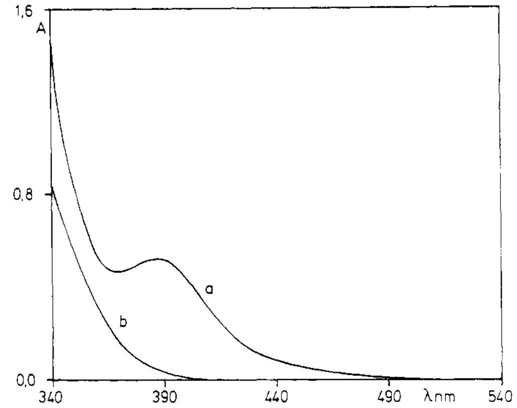

Figure 1. Electronic absorption spectra of 1.94 × 10^{-4} M $[Co(CO)_3(PPh_3)_2][Co(CO)_4]$ (a) and 1.90 × 10^{-4} M $[Co(CO)_3(PPh_3)_2][BPh_4]$ (b) in acetone under argon (298 K, 1-cm cell).

$$(OC)_nM\text{–}M(CO)_n \xrightarrow{h\nu} 2\cdot M(CO)_n$$

$$2\cdot M(CO)_n + L \rightarrow [M^{+I}(CO)_nL]^+[M^{-I}(CO)_n]^-$$

The starting complex $M_2(CO)_{2n}$ and the ion pair $[M^{I}(CO)_nL]^+[M^{-I}(CO)_n]^-$ may be considered as alternate forms of metal–metal interaction. In the dinuclear complex this interaction leads to the appearance of a $\sigma\sigma^*$ (M–M) band

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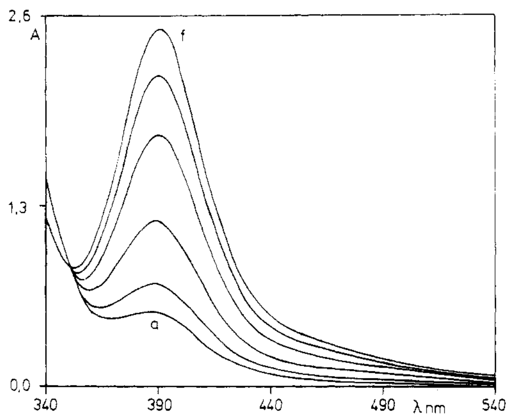

Figure 2. Spectral changes during the photolysis of 2.08×10^{-4} M $[Co(CO)_3(PPh_3)_2][Co(CO)_4]$ in acetone under argon at (a) 0- and (f) 100-min irradiation time, with $\lambda_{irr} = 405$ nm and a 1-cm cell.

in the absorption spectrum. The ion pair is expected to display outer-sphere metal to metal charge transfer (MMCT) or intervalence transfer (IT) absorption bands since the ion pair is composed of a cation- and anion-containing reducing and oxidizing metal centers.[4-7]

Both excitations, $\sigma\sigma^*$ of the dimer as well as IT of the ion pair, should then generate the same or similar radicals:

$$(OC)_nM{-}M(CO)_n + L \xrightleftharpoons{h\nu(\sigma\sigma^*)} 2{\bullet}M(CO)_n + L \xrightleftharpoons{h\nu(IT)} [M^{+I}(CO)_nL]^+[M^{-I}(CO)_n]$$

Under suitable conditions it might therefore be possible to reverse the disproportionation of metal–metal bonds photochemically. We report here a first example of the formation of a metal–metal bond induced by IT excitation of an ion pair.

The absorption spectrum of the salt $[Co(CO)_3(PPh_3)_2][Co(CO)_4]$[8-10] (Figure 1) shows a long-wavelength band at $\lambda_{max} = 386$ nm (ϵ 2500). Since $[Co(CO)_4]^-$ is colorless[11] and does not absorb above 350 nm[12] and the cation $[Co(CO)_3(PPh_3)_2]^+$[8] absorbs only below 390 nm (Figure 1), the absorption feature at 386 nm is due to the ion pair but not its components.

The new absorption band at 386 nm is logically assigned to the MMCT or IT transition from the reducing Co(–I) to the oxidizing Co(I). Such outer-sphere IT bands are rather common for ion pairs consisting of reducing and oxidizing components.[4-7] A MMCT band appears also in the spectrum of $Tl^+[Co(CO)_4]^-$.[12]

Upon MMCT excitation ($\lambda_{irr} = 405$ nm) the ion pair underwent a clean photoreaction according to

$$[Co(CO)_3(PPh_3)_2][Co(CO)_4] \rightarrow [(PPh_3)(CO)_3Co{-}Co(CO)_3(PPh_3)] + CO$$

The product $[Co_2(CO)_6(PPh_3)_2]$[8,10] was identified by its UV/visible[13] ($\lambda_{max} = 392$ nm (ϵ 23 800)) (Figure 2) and IR spectra ($\nu_{C-O} = 1950$ and 1960 cm^{-1} (KBr)).[14] At $\lambda_{irr} = 405$ nm the quantum yield of this reaction was $\Phi = 0.012$. This measurement was performed with 1.3×10^{-3} M $[Co(CO)_3(PPh_3)_2][Co(CO)_4]$ acetone solutions at 20 °C. Absorbed light intensity (1.99×10^{-9} E s^{-1} cm^{-2}) was determined by a Polytec pyroelectric radiometer that was calibrated and equipped with a RkP-345 detector. Progress of the photolysis was monitored by spectral changes at $\lambda = 392$ nm (ϵ 2400) for $[Co(CO)_3(PPh_3)_2][Co(CO)_4]$ and ϵ 23 800 for $Co_2(CO)_6(PPh_3)_2$. The total amount of photolysis was limited to 2.2% to avoid light absorption by the photoproduct.

If the photolysis was carried out at higher concentrations of the ion pair ($c > 10^{-3}$ M), the photolysis is accompanied by the precipitation of the binuclear complex. The photolysis could be thus driven almost to completion (chemical yield > 90%) due to the low solubility of $[Co_2(CO)_6(PPh_3)_2]$.[8,10]

It is suggested that the reaction proceeds by the mechanism shown in eq 1–5. The IT excitation generates a

$$[Co^{+I}(CO)_3(PPh_3)_2]^+[Co^{-I}(CO)_4]^- \xrightarrow[IT]{h\nu} [Co^0(CO)_3(PPh_3)_2][Co^0(CO)_4] \tag{1}$$

$$[Co^0(CO)_3(PPh_3)_2][Co^0(CO)_4] \rightarrow [Co^0(CO)_3(PPh_3)]_2 + [Co^0(CO)_4] \tag{2}$$

$$[Co^0(CO)_3(PPh_3)_2] \rightarrow [Co^0(CO)_3(PPh_3)] + PPh_3 \tag{3}$$

$$[Co^0(CO)_4] + PPh_3 \rightarrow [Co^0(CO)_3PPh_3] + CO \tag{4}$$

$$2[Co^0(CO)_3(PPh_3)] \rightarrow [(PPh_3)(CO)_3Co{-}Co(CO)_3(PPh_3)] \tag{5}$$

redox isomer by optical electron transfer (eq 1). The neutral radicals may diffuse apart (eq 2). These radicals are certainly labile toward substitution or dissociation (eq 3 and 4).[1-3,15] Combination of the radicals yields the stable dimer (eq 5). The low quantum yield of the photoreaction may be due to a competing reversal of some of these processes including back electron transfer within the primary radical pair. At some stages of this mechanism a modified reaction path is certainly possible.[15] For example, it has been suggested that the $Co(CO)_4$ radical may dissociate into $Co(CO)_3$ and CO.[15] The fragment $Co(CO)_3$ may then pick up PPh_3 to produce $Co(CO)_3PPh_3$ which undergoes the dimerization to the stable product.

In the context of our observations it is also of interest that under suitable conditions the comproportionation of ion pairs to generate metal–metal bonds is a rather common thermal reaction.[16] Even the photoreaction we report here occurs also as an efficient thermal reaction at higher temperatures.[10] This observation is not surprising since thermal and optical electron transfers are related processes that can be explained by a common model.[4-7,17]

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Registry No. $[Co(CO)_3(PPh_3)_2][Co(CO)_4]$, 14243-08-4; $[Co_2(CO)_6(PPh_3)_2]$, 10170-27-1; Co, 7440-48-4.

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