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Paramagnetic Organometallic Complexes. Comparison of Geometric and Electronic Structures of Paramagnetic Bis(triethylphosphine)cyclopentadienylcobalt(II) Tetrafluoroborate and Diamagnetic Bis(triethylphosphine)cyclopentadienylcobalt(I)†

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Low-temperature crystallographic analyses of $(PEt_3)_2(C_5H_5)Co^I$, **1**, and $[(PEt_3)_2(C_5H_5)Co^{II}]BF_4$, **2**, reveal remarkably similar structures, with the cyclopentadienyl ring sitting on top of a CoL_2 fragment. Both approximate C_s molecular symmetry with a pseudomirror plane perpendicular to the ML_2 plane in **1** and coincident with it in **2**. Slightly longer ligand to metal contacts are found in **2** than **1**. An electronically induced distortion in the cyclopentadienyl ligand is observed in **1** but not in **2**. Complex **1** crystallizes in an orthorhombic unit cell of symmetry $P2_12_12_1$ with (at −100 °C) a = 9.416 (1) Å, b = 22.126 (2) Å, c = 9.203 (1) Å, V = 1917 (1) Å^3, and ρ (calcd) = 1.248 g cm^{-3} for Z = 4. Complex **2** crystallizes in a monoclinic unit cell of $P2_1/n$ with (at −60 °C) a = 19.626 (5) Å, b = 7.943 (2) Å, c = 14.439 (4) Å, β = 105.01 (1)°, V = 2174 (2) Å^3, ρ(calcd) = 1.366 g cm^{-1} for Z = 4. For **1**, refinement converged at R = 0.029 and R_w = 0.026 for the 2512 independent diffractometry data collected with Mo Kα radiation ($2\theta < 50°$) (number of variables refined = 321). For **2**, refinement converged at R = 0.045 and R_w = 0.045 for 4996 reflections ($2\theta < 55°$) (number of variables = 365). Perturbation theory and semiempirical molecular orbital calculations suggest reasons for geometric differences and reactivity differences including the tendency of paramagnetic species toward labile substitution and disproportionation.

Introduction

Increasing evidence that paramagnetic complexes may play an active role in a number of catalytic processes[1] has stimulated research in this area. Recently one of us reported[2] the synthesis and characterization of a series of thermally stable 17-electron cyclopentadienylcobalt complexes from one-electron oxidation of the corresponding 18-electron complexes. Comparing reactivity of the 17- and 18-electron complexes, we found (a) the latter would trimerize alkynes, as previously reported,[3] whereas the 17-electron species were inactive, and (b) the 17-electron complexes were subject to rapid disproportionation in the presence of small donor ligands such as $P(OMe)_3$ to CO(I) and Co(III) complexes, whereas the 18-electron complexes would simply substitute L at a moderate rate.

We considered that geometric as well as electronic differences may explain the reaction pathways. Low-temperature, single-crystal X-ray-diffraction studies on the 18-electron complex $[P(C_2H_5)_3]_2(C_5H_5)Co^I$, **1**, and the 17-electron complex $\{[P(C_2H_5)_3]_2(C_5H_5)Co^{II}\}BF_4$, **2**, were undertaken to explore these differences. A bonus of this study has been the finding of an electronically induced distortion in the cyclopentadienyl ring of **1**, similar to that reported by Byers and Dahl[4] in (pentamethylcyclopentadienyl)cobalt dicarbonyl.

Table I. Summary of X-ray Diffraction Results

	1	2
formula	$C_{17}H_{35}CoP_2$	$C_{17}H_{35}BCoF_4P_2$
fw	360.35	447.15
cryst system	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_1/n$
unit cell		
temp, °C	−100	−60
a, Å	9.416 (1)	19.626 (5)
b, Å	22.126 (2)	7.943 (2)
c, Å	9.203 (1)	14.439 (4)
β, deg		105.01 (1)
V, Å^3	1917 (1)	2174 (2)
Z	4	4
ρ(calcd), g cm^{-3}	1.248	1.366
cryst dimens, mm	0.30 × 0.30 × 0.31	0.30 × 0.15 × 0.40
no. of independent reflctns	2152 ($2\theta < 50°$)	4996 ($2\theta < 55°$)
no. of reflctns, $F_o^2 > n\sigma(F_o^2)$	2145 (n = 2)	2998 (n = 3)
no. of variables refined	321	366
R	0.029[a]	0.045
R_w	0.026	0.045
largest peaks in final difference Fourier, e Å^{-3}	0.15	0.41–0.55 near F's

[a] Enantiomorphic structure refined to R = 0.040.

Experimental Section

All of the crystallographic data were obtained by using a Syntex P3 diffractometer equipped with a graphite monochromator and a low-temperature system (Mo Kα radiation, λ = 0.71069 Å). The unit cell dimensions were refined from the Bragg angles of 48–50 reflections which had 2θ values between 24 and 26°. Intensity data were collected by using ω scan technique with a scan range of 1.0; backgrounds were measured at each end of the scan with ω offset by 1.0°. The intensities of four standard reflections were monitored periodically; only statistical fluctuations were noted in both cases. Psi scans for **1** showed no fluctuation in intensity; for **2**, the intensity did vary with ψ, and thus an empirical absorption correction was made (transmission factors ranged from 0.83 to 1.00).

Both structures were refined by full-matrix least-squares techniques. All positional and thermal parameters (anisotropic for Co, P, and C; isotropic for H) were included in the refinement of **1**. For **2**, Co, P, F, C, and B were refined with anisotropic

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† Contribution No. 3245.

(1) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978.

(2) McKinney, R. J. *Inorg. Chem.* **1982**, *21*, 2051–2056.

(3) (a) Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1. (b) Wakatsuki, Y.; Yamazaki, H. *Tetrahedron Lett.* **1973**, 3383. (c) Bönnemann, H. *Angew. Chem., Int. Ed.* **1978**, *17*, 505.

(4) Byers, L. R.; Dahl, L. F. *Inorg. Chem.* **1980**, *19*, 277–284.

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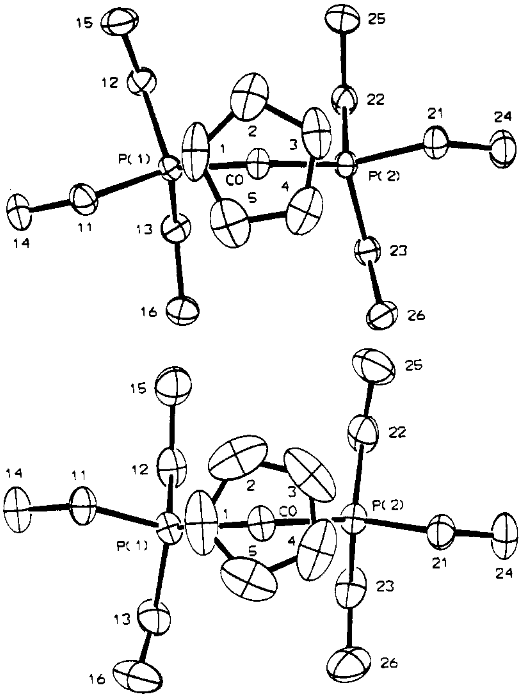

Figure 1. Comparative views of the molecule 1 and the cation 2. The average deviation of the carbon atoms from the least-squares plane in the cyclopentadienyl ring of 1 is 0.007 (2) Å and of 2 is 0.006 (2) Å. Other notable deviations from the least-squares plane of the Cp ring are as follows: for 1, Co, 1.710 (1) Å, P(1), 3.114 (1) Å, P(2), 3.082 (1) Å; for 2, Co, 1.724 (1) Å, P(1), 3.205 (1) Å, P(2), 3.064 (1) Å.

thermal parameters; the positions of the hydrogens were calculated ideally and not refined.

A summary of the crystallographic results is given in Table I. The molecular geometries are detailed in Table II and Figure 1. All other crystallographic information have been submitted as supplemental material. The mathematical and computational details of the computer software can be found elsewhere.[5]

Results and Discussion

Complexes 1 and 2 both exist as discrete molecular (or ionic) species in the crystalline state.[6] Both complexes contain a cyclopentadienyl group sitting on top of a CoL_2 fragment. Both approximate C_s molecular symmetry but appear to differ as to the orientation of the cyclopentadienyl group (see Figure 1); if we define a mirror plane perpendicular to the cyclopentadienyl group, in 1 it is nearly perpendicular to the CoP_2 plane, whereas in 2 it is nearly coplanar with the CoP_2 plane. A comparison of bond distances and angles is given in Table II and Figure 1, and we find remarkable similarity. Considering the notion that oxidation will cause a contraction of the metal orbitals, thereby causing a shortening of metal-to-ligand distances, we were somewhat surprised to find that the metal-to-ligand distances are, if anything, slightly longer in the cation 2. This may be explained if we consider the nature of the highest occupied molecular orbital (HOMO), A, which is shown in Figure 2. Note that the metal d orbital component of the HOMO is orthogonal to the Co–P bonds and therefore incapable of contributing to a σ bond. However, the symmetry does allow π interaction between the metal d orbital and a phosphorus p and/or d orbital. Whereas the contribution of this interaction is sufficiently small not to show up in the orbital plot, an examination of the wave function (LCAO) reveals that the bonding contribution does exist. Removal of an electron from this orbital decreases the amount of back-bonding from metal to phosphorus, weakening and lengthening the bond

Table II. Selected Bond Distances (Å) and Angles (deg) with Estimated Standard Deviations

	1	2
Co–P(1)	2.218 (1)	2.233 (1)
Co–P(2)	2.218 (1)	2.227 (1)
Co–P(av)	2.218	2.230
Co–C(1)	2.071 (4)	2.087 (4)
Co–C(2)	2.104 (4)	2.098 (4)
Co–C(3)	2.072 (4)	2.062 (4)
Co–C(4)	2.085 (4)	2.062 (3)
Co–C(5)	2.089 (4)	2.104 (4)
Co–C(av)	2.084	2.083
P(1)–C(11)	1.848 (3)	1.835 (3)
P(1)–C(12)	1.853 (3)	1.824 (3)
P(1)–C(13)	1.835 (3)	1.833 (3)
P(2)–C(21)	1.853 (4)	1.825 (3)
P(2)–C(22)	1.847 (3)	1.833 (3)
P(2)–C(23)	1.837 (4)	1.826 (3)
C(1)–C(2)	1.395 (7)	1.373 (6)
C(1)–C(5)	1.422 (7)	1.357 (6)
C(2)–C(3)	1.393 (6)	1.374 (6)
C(3)–C(4)	1.415 (6)	1.380 (6)
C(4)–C(5)	1.382 (6)	1.377 (6)
C–C(av)	1.401	1.372
C(11)–C(14)	1.519 (5)	1.521 (4)
C(12)–C(15)	1.512 (5)	1.530 (5)
C(13)–C(16)	1.527 (5)	1.506 (5)
C(21)–C(24)	1.517 (5)	1.524 (4)
C(22)–C(25)	1.515 (5)	1.521 (5)
C(23)–C(26)	1.518 (5)	1.517 (5)
P(1)–Co–P(2)	98.49 (3)	101.21 (3)
Co–P(1)–C(11)	113.9 (1)	113.4 (1)
Co–P(1)–C(12)	118.2 (1)	117.4 (1)
Co–P(1)–C(13)	120.8 (1)	114.8 (1)
Co–P(2)–C(21)	114.6 (1)	114.5 (1)
Co–P(2)–C(22)	119.4 (1)	115.6 (1)
Co–P(2)–C(23)	118.7 (1)	114.0 (1)
C(2)–C(1)–C(5)	109.1 (4)	109.9 (4)
C(1)–C(2)–C(3)	106.8 (5)	106.8 (4)
C(2)–C(3)–C(4)	109.0 (4)	108.1 (4)
C(3)–C(4)–C(5)	108.0 (4)	108.1 (4)
C(1)–C(5)–C(4)	107.1 (4)	107.1 (4)
P(1)–C(11)–C(14)	118.7 (3)	115.7 (2)
P(1)–C(12)–C(15)	113.4 (3)	113.4 (2)
P(1)–C(13)–C(16)	113.9 (2)	113.8 (3)
P(2)–C(21)–C(24)	118.1 (3)	115.6 (2)
P(2)–C(22)–C(25)	113.3 (3)	113.6 (3)
P(2)–C(23)–C(26)	113.3 (3)	112.6 (2)

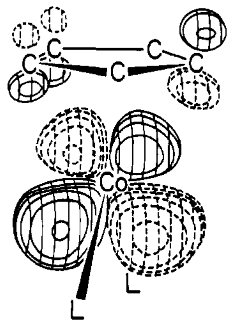

Figure 2. Molecular orbital envelope for the HOMO (A) of 1 and 2.

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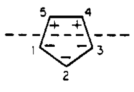
[5] Nugent, W. A.; Harlow, R. L. *Inorg. Chem.* **1979**, *18*, 2030.

[6] A crystal determination of the iodide salt [CpCo(PEt$_3$)$_2$]I was performed. The crystals are monoclinic of space group $C2/c$, at 60 °C, with a = 19.666 (4) Å b = 7.827 (3) Å, c = 14.437 (4) Å, β = 106.37 (1)°, and V = 2132 (2) Å^3. Unfortunately, the cation sits on a twofold axis of rotation, and the Cp group is thus disordered. Attempts to model the disorder were not completely successful. The best refinement converged at R = 0.091 using 1956 reflections with $I > 3\sigma(I)$. Two values perhaps worth noting are the Co–P distance of 2.215 (1) Å and the P–Co–P′ angle of 102.4 (1)°.

slightly. This then is a molecular orbital description of the "hardening" of the metal upon oxidation, making it less compatible with the "soft" ligands PR_3 and $C_5H_5^-$. The slight enlarging of the P–Co–P angle may also reflect the decrease in this π interaction which would have optimum overlap at much smaller P–Co–P angle but would be much more sterically congested, which is, of course, the driving force for opening the angle.

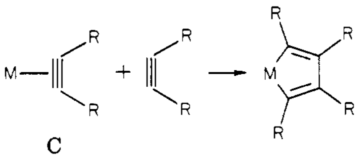
Cyclopentadienyl Ring Distortion. Note the systematic variation of carbon–carbon distances in the cyclopentadienyl group of **1**. The long distances C(1)–C(5) and C(3)–C(4) coupled with the shorter distances C(1)–C(2)–C(3) and C(4)–C(5) give a very clear picture of the "allyl–ene" distortion previously described by Byers and Dahl[4] for $(Me_5C_5)Co(CO)_2$ (the theoretical reasons for this distortion were also discussed and apply here). However, note also that the cyclopentadienyl ring of the cation **2** reveals no such variation; the distances are equal within experimental error. This is consistent with the theoretical picture described by Byers and Dahl; the distortion is the result of the cyclopentadienyl component of the HOMO having the symmetry indicated in B (you can see an indication of it in Figure 2). Removal of electrons from the HOMO would therefore reduce the antibonding between C(1)–C(5) and C(3)–C(4) and correspondingly reduce bonding between C(1)–C(2)–C(3) and C(4)–C(5), i.e., change toward equalization of the C–C distances.



B

Reactivity Differences. Though we have observed and explained some subtle differences between diamagnetic **1** and paramagnetic **2**, they would not seem significant enough to account for the reactivity differences described in the introduction. We must, therefore, examine electronic differences that may not appear in the ground-state geometry.

The differences in the catalytic trimerization of alkynes is easily accounted for if we remember that the accepted mechanism[3] includes the formation of a metallacyclobutadiene, D; D then reacts with another alkyne to give a product. However, the conversion of C to D requires a formal two-electron oxidation of the metal (a so-called oxidative addition). For an 18-electron Co(I) species like **1**, this involves a conversion to a formal Co(III) species, but for 17-electron Co(III) species like **2**, it would require a very unlikely Co(IV) intermediate.



C

D

The substitutional lability and tendency toward disproportionation generally associated with paramagnetic complexes and observed for **2** and related species is not so readily accounted for. Using semiempirical molecular orbital calculations,[7] we have probed both dissociative and associative pathways for the substitution of $(CpCoL_2)^x$ for x = 0–2. In essence, we are exploring how the occupation of the MO A will affect either of these substitution pathways; A is doubly occupied, singly occupied, and unoccupied, respectively, in the three cases. CpCoL and $CpCoL_3$ represent possible intermediates or transition states in the substitution pathway. The results are given in Table III. We remind the reader that the absolute magnitude of the calculated energy differences are unreliable in the extended Hückel formalism but that the trends in closely related series are useful.[8]

Table III. Calculated Energies of Dissociation and Association for $[CpCoL_2]^x$

$$[CpCoL]^x \xleftarrow{-L} [CpCoL_2]^x \xrightarrow{+L} [CpCoL_3]^x$$

	ΔE, eV	
x	dissociatn	associatn
0	1.7	1.3
1	1.6	0.3
2	1.6	-1.1

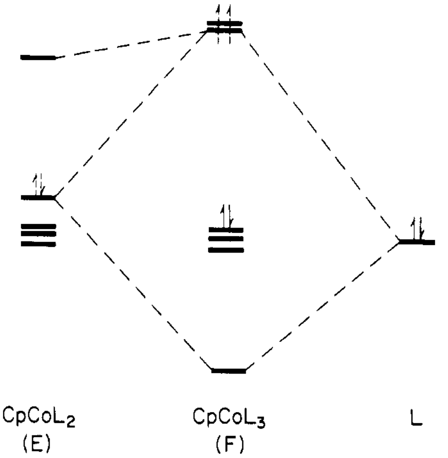
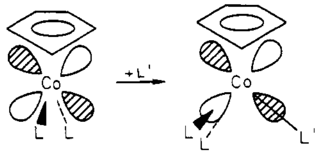


Figure 3. Qualitative molecular orbital energy diagram for $CpCoL_2$ and $CpCoL_3$.

The dissociative pathway is calculated to be unaffected, but the associative pathway is strongly affected by the occupation of A. The lack of effect in the dissociative case may be traced to the relatively small involvement of A in the bonding between Co and P, as described above. The small change observed in the Co–P distances in the molecular structures supports the idea that there is only a very weak contribution from the π interaction to Co–P bonding and we might expect very little effect on the dissociation energy.

However, the strong effect of HOMO (A) occupation on the associative pathway may also be attributed to its symmetry (Figure 2). An approaching free ligand will strongly perturb the HOMO as illustrated in E → F, resulting in a MO energy diagram change as shown in Figure 3. It becomes obvious that in the x = 0 (A doubly occupied) case a substantial barrier to achieving the $CpCoL_3$ intermediate is expected; the dramatic increase in energy of the two A electrons concomitant with the energy costs



E

F

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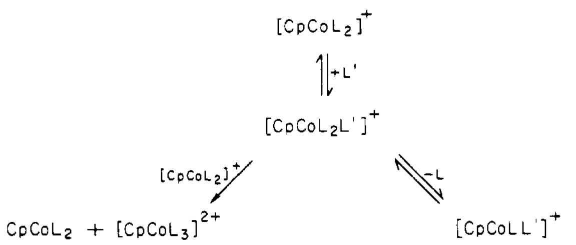
(7) The semi-empirical technique used is similar to the extended Hückel technique (Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. Hoffman, R.; Lipscomb, W. N. *Ibid.* **1962**, *36*, 2179, 3489; *37*, 2872) but includes a correction for two-body repulsion (Anderson, A. B. *Ibid.* **1975**, *62*, 1187). The parameter set is that described previously (Pensak, D. A.; McKinney, R. J. *Inorg. Chem.* **1979**, *18*, 3407).

(8) McKinney, R. J.; Pensak, D. A. *Inorg. Chem.* **1979**, *18*, 3413.

Scheme I



of reorganizing the ligands is not offset by the lowering energy of the two phosphorus donor electrons. In the $x = 2$ (A unoccupied) case, a clear net bonding interaction is achieved leading to a gain in energy. It is not surprising then that the $x = 1$ (singly occupied) case is between these two extremes, i.e., the energy loss of raising one electron plus the reorganization energy is just about offset by the lowered energy of the two phosphorus electrons; this leads to a much lower barrier (or maybe none) for the associative substitution pathway in the paramagnetic complex. Similar calculations have been carried out for other simple paramagnetic complexes such as the 17-electron complex $Mn(CO)_5$, and we obtain the same result and explanation; i.e., dissociative substitution may not be significantly different for the 17- and 18-electron complexes, but associative substitution can be expected to be significantly easier in 17-electron complexes.

Very similar arguments can explain the rapid disproportionation we observe in the presence of a small donor ligand such as $P(OMe)_3$. If the intermediate F is generated, then the singly occupied HOMO of F may be of sufficiently high energy (see Figure 3) to transfer the electron to the lower singly occupied HOMO of the starting complex E, resulting in disproportionation as indicated in Scheme I.

Registry No. 1, 79639-49-9; 2, 80719-10-4; $[CpCo(PEt_3)_2]I$, 80719-08-0.

Supplementary Material Available: Tables of positional and thermal parameters, general temperature factor expressions, and structure factor amplitudes for 1 and 2 and a stereoscopic crystal packing digram for 2 (29 pages). Ordering information is given on any current masthead page.

Metal–Metal Double Bond Formation via Steric Design. Synthesis and X-ray Crystal Structure of $[Rh(\mu\text{-}t\text{-}Bu_2P)(CO)(PMe_3)]_2(Rh{=}Rh)$

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$[Rh(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$ reacts with neat PMe_3 at room temperature to give $[Rh(\mu\text{-}t\text{-}Bu_2P)(CO)(PMe_3)]_2$ (3) quantitatively. 3 contains two Rh(I) atoms bridged by two $t\text{-}Bu_2P$ ligands. Each Rh carries one terminal CO and one PMe_3 ligand and has a distorted tetrahedral geometry. The Rh–Rh distance (2.550 (1) Å) and diamagnetism are consistent with a metal–metal bond of order 2. The structure has been determined by a single-crystal X-ray diffraction study. Crystal data for 1: $C_{24}H_{54}O_2P_4Rh_2$, $M = 704.40$, monoclinic, $P2_1/n$, $a = 10.791$ (7) Å, $b = 11.206$ (7) Å, $c = 14.398$ (8) Å, $\beta = 105.915$ (5)°, $U = 1674.3$ (5) Å^3, $D_{calcd} = 1.397$ g cm^{-1}, $Z = 2$ (dimers), λ(Mo K_α) = 0.710 69 Å (graphite monochromator), μ(Mo K_α) = 11.8 cm^{-1}. Refinement of 2078 observed ($I > 2\sigma(I)$) reflections (2801 measured) gave a final $R = 0.0366$ and $R_w = 0.0434$.

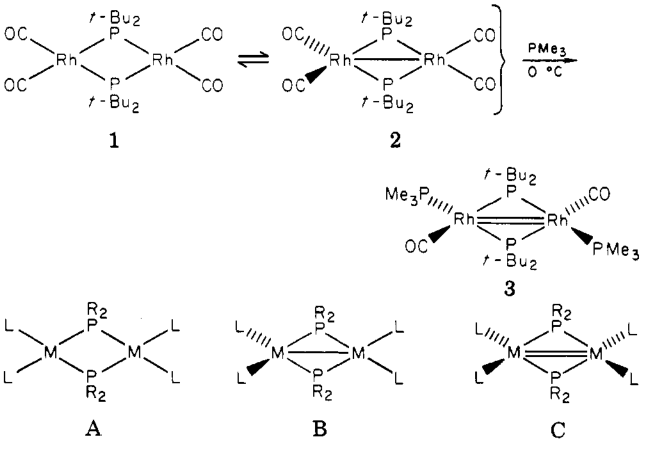
Introduction

There are many examples where the addition of a Lewis base such as a phosphine (PR_3) or isocyanide (CNR) to a dinuclear or polynuclear complex results in the formation of species of lower nuclearity. This is often accompanied by the cleavage of a metal–metal bond if one is present in the original complex.[1]

We report here an example of a reaction in which the bond order between two metals in a dimer apparently increases upon addition of a Lewis base. The transformation occurs by simply changing the steric bulk of the terminal ligands.

As part of a study of the steric effects of phosphido (R_2P^-) ligands in organometallic chemistry, we recently described an unusual dinuclear Rh(I) system that exhibits the interesting feature of a facile reversible metal–metal

Scheme I[a]



[a] M = Co, Rh, Ir; L = two-electron donor, CO, PR$_3$, etc.

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[1] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; see chapters 3, 4 and 26 and references therein. For recent developments in complexes with metal–metal bonds see also: Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982. Chisholm, M. H., Ed. "Reactivity of Metal-Metal Bonds"; American Chemical Society: Washington DC 1981; *ACS Symp. Ser. No. 155.*

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