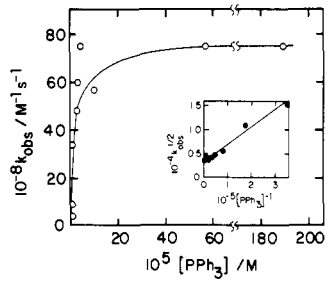

Figure 1. Illustrating the phosphine dependence of the observed pseudo-second-order rate constant for dimerization according to eq 5.

exist in equilibrium, but only the latter is reactive toward dimer formation:

$$Rh(dmgH)_2 + PPh_3 \overset{K_{45}}{\rightleftharpoons} Rh(dmgH)_2PPh_3 \quad (3)$$

$$2Rh(dmgH)_2PPh_3 \xrightarrow{k_{55}} [Rh(dmgH)_2PPh_3]_2 \quad (4)$$

$$-\frac{d[Rh(dmgH)_2PPh_3]}{2dt} = \frac{k_{55}}{(K_{45}^{-1}[PPh_3]^{-1} + 1)^2}[Rh(dmgH)_2PPh_3]^2 \quad (5)$$

A least-squares analysis of the dependence of k_d upon [PPh_3] according to eq 5 affords the values $2k_{55} = 7.5 \times 10^8$ M^{-1} s^{-1} and $K_{45} \sim 10^5$ M^{-1}. We conclude that the pathway shown by eq 4 predominates over those in which the reactants are two four-coordinate Rh(II) species or one of each (i.e., $k_{55} >> k_{44}, k_{45}$).

Further corroboration that the transient is indeed, the indicated monomeric rhodium(II) complex came from trapping experiments with such reagents as iron(III) chloride. These studies were necessarily limited to the use of the organorhodoxime as the starting material, since the rhodium(II) dimer reacts thermally as discussed below. Addition of iron(III) chloride prior to photolysis of isopropylrhodoxime results in total conversion of the transient to a rhodium(III) complex, chloro(triphenylphosphine)rhodoxime:

$$Rh(dmgH)_2PPh_3 + FeCl_3 \rightarrow ClRh(dmgH)_2PPh_3 + FeCl_2 \quad (6)$$

A thermal reaction between the dimer and iron(III) chloride also occurs (eq 7). The reaction rate, easily determined by using

$$[Rh(dmgH)_2PPh_3]_2 + 2FeCl_3 = 2ClRh(dmgH)_2PPh_3 + 2FeCl_2 \quad (7)$$

conventional techniques, is first order with respect to the concentration of the dimer but independent of [Fe^{3+}] ($9 \times 10^{-5} - 1.8 \times 10^{-3}$ M), [H^+], and [Cl^-]. The rate constant is $k_1 = 5.8 \times 10^{-2}$ s^{-1} (ethanol, 25.0 °C) or 9.8×10^{-2} s^{-1} (THF, 25.0 °C). Determinations of the rate constant as a function of temperature (8–25 °C) in ethanol yield the activation parameters $\Delta H_1^{\ddagger} = 85.6 \pm 2.6$ kJ mol^{-1} and $\Delta S_1^{\ddagger} = 19.2 \pm 7.7$ J mol^{-1} K^{-1}. Use of $Fe(NO_3)_3$, $Fe(ClO_4)_3$, or $Fe(phen)_3Cl_3$ gave identical rate constants, although after consumption of the Rh(II) dimer was complete, further small absorbance changes were noted which could be attributed to substitution reactions of an axial ligand on the Rh(III) rhodoxime product. The kinetic data are explained by a mechanism consisting of the rate-limiting thermal dissociation of the dimer (eq 1) followed by its rapid oxidation (eq 6). On the basis of the value of k_1 and k_{55} for eq 4, the equilibrium constant[9] between dimer and monomer in ethanol is 1.5×10^{-10} M at 298 K, with $\Delta S° \sim 100$ J mol^{-1} K^{-1} and $\Delta H° \sim 86$ kJ mol^{-1}. The large positive value of $\Delta S°$ is consistent with the monomerization process.

If solvent effects are ignored, the estimate of $\Delta H°$ may be taken as an estimate of the metal–metal bond dissociation enthalpy in the dirhodium complex for which the Rh–Rh bond distance[3] is 2.97 Å. By way of comparison the bond energies and bond lengths of other Rh–Rh bonds are rhodium metal,[10] 93 (2.68); $Rh_4(CO)_{12}$, 91[11] and 114[10] (2.73); $Rh_6(CO)_{16}$, 89[11] and 114[11] kJ mol^{-1} (2.78 Å). Comparisons with other dimeric d^7 complexes can also be made: the mass spectrometric value[12] for homolytic dissociation of $Tc_2(CO)_{10}$ is 177 kJ mol^{-1}, compared to $\Delta H^{\ddagger} = 160$ kJ mol^{-1} from a kinetic study in decalin[13]. That the Tc–Tc bond is much stronger than the Rh–Rh bond is not unexpected in view of the much smaller degree of ligand–ligand repulsions in the former.[14]

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(9) The rate constants for the dimer (D) to monomer (M) interconversion are those defined by the rate law

$$-d[D]/dt = d[M]/2dt = k_1[D] - k_{55}[M]^2$$

The equilibrium constant for the reaction D ⇌ 2M is $K = k_1/k_{55}$.

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Synthesis and Molecular Structure of the Dissymmetric Mo≡Mo Compound $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3(C_6H_5P(OCH_2CH_2)_2NH)]$: First Example of Direct CO Substitution in $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_2$

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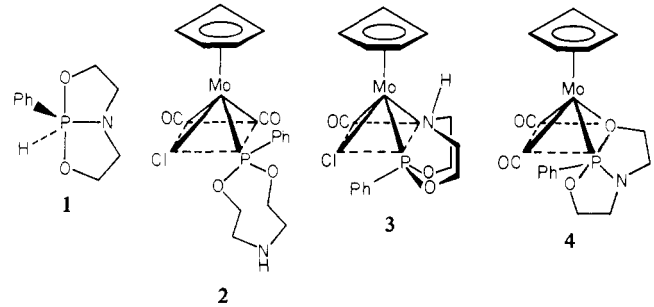
The bicyclophosphorane **1** (phoran) is the precursor of a multidonor site ligand, which, in its open tautomeric form, was found to coordinate transition metals[1] either via the triply coordinated phosphorus alone, as in **2**, or via both the triply coordinated phosphorus and nitrogen atoms as in 3. More recently, the



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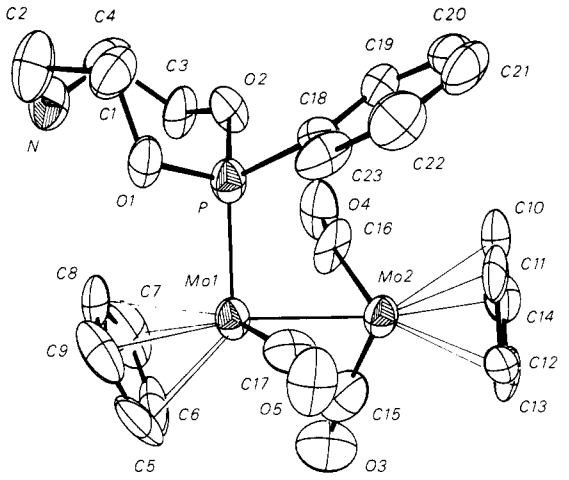

Figure 1. Molecular structure of $(\eta\text{-}C_5H_5)_2Mo_2(CO)_3$(phoran). Bond lengths: Mo1–Mo2, 2.506 (1); Mo1–P, 2.383 (4); Mo2–C15, 1.870 (24); Mo2–C16, 1.940 (15); Mo1–C17, 1.925 (15); Mo1–C15, 2.738 (17); Mo1–C16, 2.646 (18); Mo2–C17,2.495 (16); Mo1–Cp (mean), 2.312 (7); Mo2–Cp (mean), 2.335 (6) Å. Bond angles: Mo1–Mo2–C15, 75.9; Mo1–Mo2–C16, 71.7; Mo2–Mo1–C17, 67.0; Mo2–Mo1–P, 92.3; Mo2–Mo1–Cp, 154.6; Mo1–Mo2–Cp, 163.8°; angle between the planes C17–Mo1–Mo2 and Mo1–Mo2–C16, 155.5°.

bicyclo, trigonal-bipyramidal tautomer has been found in a novel type of complex (**4**). The latter complex is the first known to contain a phosphoranide ligand.[2]

To explore the bridging abilities of this ligand toward multiply bonded metal–metal compounds, we chose $(\eta^5\text{-}C_5H_5)(CO)_2Mo{\equiv}Mo(CO)_2(\eta^5\text{-}C_5H_5)$[3] (**5**) as a substrate. This selection derives from our prior interest in the latter compound, the reactivity of which toward chelating ligands has not yet been investigated.

The chemistry of **5** heretofore has been characterized by vicinal or geminal addition of both nucleophiles and electrophiles to the metal–metal triple bond, resulting in a decrease in the Mo≡Mo bond order from 3 to 1.[4-6] Thus phosphanes, phosphites, disulphides, alkynes, allenes, aminocyanamides, iodine, hydrochloric acid, etc., add to the metal–metal link to produce "symmetrical" dimers. It should be pointed out that even when only 1 molar equiv of PPh_3 or $P(OMe)_3$ is allowed to react with the Mo≡Mo dimer, one nevertheless obtains 0.5 equiv of the vicinal bis adduct, plus 0.5 equiv of nonreacted starting material. These same compounds can often also be obtained by substitution reactions of CO from $[CpMo(CO)_3]_2$.[4,7a] A second characteristic of **5** is that no example of *direct substitution* of a carbonyl ligand, with retention of the Mo≡Mo bond, seems to have been described yet. In the only instance where an unsymmetrical Mo≡Mo derivative, $Cp_2Mo_2(CO)_3(PPh_3)$, was obtained, it did not result from substitution but from thermal elimination of PPh_3 and CO from $[CpMo(CO)_2(PPh_3)]_2$.[4]

The reaction between **1** and **5** contradicts both characteristics of the chemistry of **5**. We obtained no evidence for the expected formation of a dinuclear molybdenum compound having both metals bridged by ligand **1**. Moreover, we did observe the unexpected formation, *at room temperature* and as a stable major species (40% of the crude reaction mixture), of the substitution compound **8**. This complex derives from the open-form tautomer of **1**, retains the metal–metal triple bond, and is the first example of CO substitution in **5**.

Compound **5** was completely consumed after 12 h when stirred at room temperature with an equimolar amount of **1** in a toluene/ether mixture. A minor amount (ca. 15%) of red crystalline product, which is sparingly soluble in common solvents, precipitated. It is formulated as the conventional product $[CpMo(CO)_2(phoran)]_2$ (**6**); a trans configuration is proposed[7] for it on the basis of the infrared (δ_{NH} 3380, ν_{CO} 1870 cm^{-1}, KBr) and ^1H NMR spectra (δ_{C5H5} 4.88, J_{PH} = 2.5 Hz, $CDCl_3$). The two main products of the reaction were isolated by column chromatography (on silica) of the filtrate and identified as $Cp_2Mo_2(CO)_5$(phoran) (**7**) and $Cp_2Mo_2(CO)_3$(phoran) **8**, respectively, the latter being slightly predominant. Each exhibits its parent ion in the field-desorption mass spectrum obtained from acetone solution.[8]

Characteristic of $Cp_2Mo_2(CO)_5$(phoran) are the IR absorptions at 3400 (ν_{NH}) and 1973, 1963 (sh), 1906, 1887, and 1843 cm^{-1} (ν_{CO}, CH_2Cl_2). There are two signals for the C_5H_5 groups in the ^1H spectrum (δ^2 4.92, δ^1 5.14, $^3J_{PH}$ = 1.2 Hz, $CDCl_3$) and one signal in the ^{31}P NMR spectrum (72.9 ppm).

By contrast, $Cp_2Mo_2(CO)_3$(phoran) contains three CO groups with IR frequencies at 1878 and 1979 cm^{-1} (CH_2Cl_2); ν_{NH} is found at 3373 cm^{-1}. The ^1H NMR signals of the C_5H_5 protons in **8** are inverted compared with **7** (δ^1 4.71, δ^2 5.05, $J_{P\text{-}CH}$ = 1.7 Hz, $CDCl_3$) and the ^{31}P signal is toward lower fields (82.0 ppm, $^3J_{PH}$ = 1.7 Hz, $CDCl_3$) compared to the former complex. In contrast to the light-sensitive $Cp_2Mo_2(CO)_3(PPh_3)$,[4] compound **8** (not light sensitive) is directly accessible from $Cp_2Mo_2(CO)_4$; it therefore appears to be the first stable, dissymetric derivative of the type $Cp_2Mo_2(CO)_3L$, where L is a nucleophile or a π-coordinated ligand. Thus it fills the gap between $[CpMo(CO)_2L]_2$[4-6] and $[CpMo(CO)L]_2$.[9] It must be emphasized that the conversion of **7** into **8** can only be realized by heating to 100–130 °C for 12 h, while the direct formation of **8** from **5** was observed to occur at room temperature in otherwise similar conditions.

The structure of $Cp_2Mo_2(CO)_3$(phoran) has been established by X-ray diffraction methods and was solved by conventional heavy-atom methods. The red-brown monoclinic crystals crystallize in the space group $P2_1/c$, cell constants a = 14.902 (3), b = 16.681 (3), c = 9.631 (2) Å; β = 104.84 (2)°; V = 2314 Å^3; Z = 4. Of 2665 measured reflections (Cu radiation, λ = 1.5418 Å, Ni filter), 1625 with $\sigma(I)/I < 0.33$ were used for the refinement of the structure (R_F value = 0.067).

The molybdenum–molybdenum bond length is only slightly affected by the substitution (2.506 compared to 2.448 Å in the parent compound),[11] which confirms its triple bond character. The P–Mo bond (2.38 Å) is short when compared to the range (2.44–2.52 Å) found, for example, in phosphine or phosphite adducts of mononuclear molybdenum(II) complexes containing the $CpMoPR_3$ moiety (R = OCH_3, C_6H_5).[10] The introduction of the phosphorane ligand causes some bending of the Cp–Mo–Mo–Cp axis as well as an average 0.2 Å shortening of the Mo–CO bonds when compared with the parent compound, probably as a result of increased electron density at these groups. The "semibridging" carbonyls[9,11] are more dissymmetrically positioned than in the parent compound. This parallels the unusually low (ν_{CO}) absorption frequencies observed in the infrared.

No proof for an adduct in which **1** behaves as a bridging ligand has been found yet. Compound **8** is expected to have a highly reactive metal–metal triple bond, and its chemistry is under investigation.

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Similar behavior, i.e., formation of the dissymetric substitution product at room temperature, was also observed when **1** was allowed to react with the pentamethylcyclopentadiene analogue $[(C_5Me_5)Mo(CO)_2]_2$.

Acknowledgment. J. W. thanks Professor H. Brunner for generous support of part of this work.

Supplementary Material Available: A table of atomic positions and thermal parameters and a table of bond lengths and angles (4 pages). Ordering information is given on any current masthead page.

Electrochemically Activated Binding of Benzo[*a*]pyrene and 6-Methylbenzo[*a*]pyrene to DNA

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Chemically activated and enzymically activated binding of benzo[*a*]pyrene (B[*a*]P) to DNA have been reported by using iodine,[1,3] hydrogen peroxide,[1-3] and horseradish peroxidase.[4] We wish to report a binding of B[*a*]P to DNA activated by electrochemical oxidation of B[*a*]P. Previous activation methods have relied on oxidations in homogeneous solutions by using oxidants of fixed redox potential, while electrochemical activation allows the variation of potential. Also, previous methods have required the oxidant to be in direct contact with the DNA, which is not a requirement for electrochemical activation. These advantages, although not fully exploited in this first report, have motivated this work.

These experiments have been carried out in 50% ethanol solution prepared by mixing equal volumes of 0.6 mM heat-denatured calf thymus DNA (Sigma Chemical Co., St. Louis, MO) in 0.01 M (in Na^+) phosphate buffer (pH 6.8) with a 100% ethanol solution of 0.10 M tetra-*n*-butylammonium perchlorate (TBAP, Southwestern Analytical Chemicals, Austin, TX) and 0.20 mM hydrocarbon. The electrolysis was performed in a three-chamber (working electrode, buffer, and auxiliary electrode chambers) Coulometric cell with 50% ethanol solution containing buffer and TBAP only in the buffer and auxiliary chambers. A potential was applied to a Pt gauze electrode vs. an Ag-wire pseudoreference electrode, and the auxiliary electrode was Pt wire. Standard electrochemical instrumentation which has been described elsewhere was used.[5] The potential was set to approximately 100 mV anodic of the cyclic voltammetric peak potential reported by us in acetonitrile vs. Ag.[6,7] The solution was stirred by using a magnetic stirrer; argon was bubbled continuously, and the entire cell was shielded from room light.

At the end of 2 h, the DNA solution was stored at −15 °C for 1 h to precipitate part of the TBAP and the DNA associated with it, which was then filtered at the same temperature. For a typical solution volume of 30 mL, 10 mL of 0.01 M phosphate buffer was used to suspend the wet crystals, and this slurry was stored at 4 °C for 2 h, at which time 10 mL of chloroform was added to dissolve the TBAP. The whole solution was then stored at 4 °C for an additional hour; the aqueous layer was drawn off and washed until no fluorescent compounds were detected. This was usually accomplished by washing 4 times with buffer-saturated chloroform and then washing 10 times with buffer-saturated ethyl acetate. Finally, UV absorbance spectra were recorded in a Cary 219 spectrophotometer and fluorescence spectra on an Aminco-Bowman spectrophotofluorometer. Excitation spectra were corrected for nonuniform lamp intensity by using power data from a rhodamine B quantum counter measured with an International Light Model 700 radiometer.[8]

A similar experiment was run by using 0.1 mM (in 50° ethanol) 6-methylbenzo[*a*]pyrene kindly furnished by Professor G. H. Daub of our department. A control experiment using 0.1 mM B[*a*]P was run in which the solution was merely stirred at room temperature for 2 h and shielded from light, although not bubbled with argon.

The fluorescence excitation spectrum for DNA which was stirred with B[*a*]P and washed as described above (Figure 1a) exhibits a maximum at 290 nm which corresponds to the absorption maximum for B[*a*]P at 296 nm (ϵ 3922 L mol^{-1} cm^{-1}) and exhibits an emission peak at 420 nm which corresponds to the emission peak at 418 nm obtained in ethanol for B[*a*]P. Thus the spectra are not red shifted appreciably, although the fine structure has been lost. However, the excitation and emission peaks found for the electrolyzed B[*a*]P product at 330 and 435 nm, respectively (Figure 1b), are red shifted, indicating chemical perturbation of the aromatic system. These wavelengths are similar to those obtained in previous fluorescence studies of chemically activated and in vivo binding.[3,9] This experiment was run as a blank to the experiments that follow.

The excitation spectrum for the electrolyzed 6-MeBa[*a*]P (figure 1c) shows a strong blue shift to 250 nm from the ethanol-solution absorption peak at 300 nm. The emission maximum at 410 nm is also blue shifted from its solution value of 423 nm. The blue shift found for the excitation peak could have arisen from an inaccuracy in the spectrum correction procedure or could indicate a condition of electron withdrawal from the aromatic system upon binding. We might also point out that possible excitation peaks near 400 nm might have been lost due to the intense scattering of the instrument used.

It may be noticed that the signal level for the 6-MeB[*a*]P–DNA emission peak is of the same order of magnitude as that for the DNA control. However, the amount of DNA recovered, as assayed by absorbance at 261 nm, was much less with the 6-MeB[*a*]P experiment. One way of correcting for DNA recovery, which also provides a rough estimate of the extent of binding, is to assume that the fluorescence quantum yield for hydrocarbon is unchanged after incorporation into DNA, an assumption which is not unreasonable, at least for 6-MeB[*a*]P.[4] This assumption allows us to calculate a minimum level of binding (MLB) in numbers of hydrocarbons bound per nucleotide unit

$$\mathrm{MLB} = I_{em} F \epsilon / A_{261} \qquad (1)$$

where I_{em} is the fluorescence emission intensity measured in μV (arbitrary units) when excited at the excitation maximum (uncorrected), F is a conversion factor relating concentration of hydrocarbon to emission intensity under identical spectrophotometric conditions (mol L^{-1} μV^{-1}), ϵ is molar absorptivity for DNA at 261 nm, and A_{261} is absorbance of DNA. MLB values for the three experiments are listed in Table I; 1/MLB values are also listed.

The level of enhancement of fluorescence signal over simple physical binding is then better than a factor of 10 in these experiments and is comparable to levels achieved by other workers using I_2 activation.[2] For the sake of comparison, we ran an I_2-activated experiment by using the same reagent concentrations listed above plus 5 mM (in I) I_2 and achieved a MLB value of 9-μmol B[*a*]P per mol of nucleotide (using phenol washing and subtracting phenol-washed blank) as compared to about 3000 for calf thymus DNA quoted by Hoffmann et al.[2] However, they

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