calculated, computational time may be saved in evaluating the partial derivatives by using the relationships

$$\delta FM/\delta M = -\{[M] + [MA] + [MA_2] + [MB] + [MB_2] + [MAB] + [MHAB]\}/[M]$$

$$\frac{\delta FM}{\delta A} = -\frac{[MA] + 2[MA_2] + [MAB] + [MHAB]}{[A]}$$

$$\frac{\delta FM}{\delta B} = -\frac{[MB] + 2[MB_2] + [MAB] + [MHAB]}{[B]}$$

$$\frac{\delta TA}{\delta M} = -\frac{[MA] + 2[MA_2] + [MAB] + [MHAB]}{[M]} = \frac{\delta FM}{\delta A}\frac{[A]}{[M]}$$

The calculations given in Table III were made by using the constants given in Table I and total concentrations appropriate to the different stages in the reaction.

Before the solution was mixed, the concentrations of free PLP and PLPEta Schiff bases in the preequilibrated Schiff base reactant solution were calculated from the known total concentrations of PLP and Eta and the pH at which the solution was equilibrated. For the time a few milliseconds after mixing this Schiff base solution with an equal volume of Zn(II) and aminoacidate solution, the unit species were taken as Zn(II), PLP^{3-}, $PLPEta^{3-}$, Aa^{i-}, and H^+. The total concentrations of PLP and PLPEta were taken as half the concentrations of uncombined PLP and Schiff base in the initial reactant solution containing these species. The total concentrations of Zn(II) and Aa^{i-} were taken as half the total concentrations in the other reactant solution. $[H^+]$ was determined from the measured pH of the mixed solution because the pH remains essentially constant during imine exchange.

The concentrations for the final equilibrium state of the mixed solutions were calculated by using half the total concentrations of the PLP, Eta, Zn, and aminoacidate in the initial solutions before mixing. The measured pH was used to obtain $[H^+]$.

As a point of additional interest, if the pH of the reactant solution is not known independently, $[H^+]$ may be computed by adding to the above a mass balance equation on total titratable H^+, e.g., $TH = [H^+] - [OH^-] + [HA] + 2[H_2A] + [HB] + 2[H_2B] + [HAB] + [MHAB]$.

Registry No. Ethylamine, 75-04-7; alanine, 56-41-7; aspartic acid, 56-84-8; $HPLPEta^{2-}$, 85535-42-8; $H_2PLPEta^-$, 85535-40-6; $H_3PLPEta$, 64818-26-4; PLP, 54-47-7; Zn^{2+}, 23713-49-7; PLP^{3-}, 85535-41-7; Ala^-, 17807-53-3; Zn(PLPEtaH), 85552-60-9; $HPLPAla^{3-}$, 85535-43-9; $H_2PLPAla^{2-}$, 85535-44-0; $Zn(PLPAla)^{2-}$, 85115-54-4; $Zn(HPLPAla)^-$, 85552-61-0; $Zn(H_2PLPAla)$, 85552-62-1; $Zn(Ala)^+$, 12542-92-6; $Zn(Ala)_2$, 14647-06-4.

Communications to the Editor

Ortho-Metallation at a Multiply Bonded Dirhenium Center: The First Such Example Occurring at a Multiple Bond of the M_2L_8 Type

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Bidentate bridging ligands such as bis(diphenylphosphino)methane (dppm) that contain a single bridgehead atom have proven to be very effective in stabilizing molecules containing pairs of multiply bonded metal atoms.[1] In exploring the behavior of other bridging ligands of this general type, including those in which the ligand is unsymmetrical, we turned our attention to 2-(diphenylphosphino)pyridine (Ph_2Ppy). Prior work by Balch and co-workers[2-5] has demonstrated the effectiveness of Ph_2Ppy in stabilizing well defined homo- and heterobinuclear transition-metal complexes, particularly those of the group 8 metals. The extension of these studies to include multiply bonded pairs of atoms of the early transition series is especially noteworthy as judged by the recent results we have obtained on dirhenium complexes of this ligand. In the course of these investigations, we have isolated a derivative of the triply bonded Re_2^{4+} core,[1,6-9] possessing the stoichiometry $Re_2Cl_3(Ph_2Ppy)_2[(C_6H_5)(C_6H_4)Ppy]$ (**1**). This complex contains a novel tridentate bridging mode for this ligand in which ortho metalation has occurred at one of the phenyl rings. This is, to our knowledge, the first example of an ortho-metalation reaction involving a multiply bonded dimetal unit contained within an M_2L_8 skeleton. This result has an important bearing in the

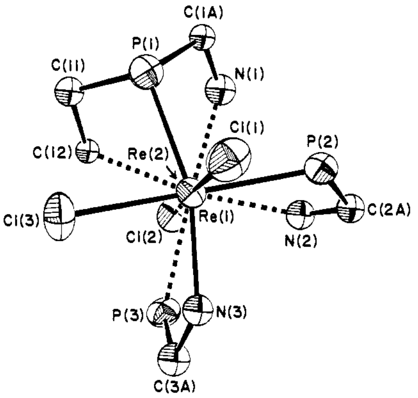

Figure 1. ORTEP drawing of the central part of the $Re_2Cl_3(Ph_2Ppy)_2[(C_6H_5)(C_6H_4)Ppy]$ molecule (1). The view is straight down the Re-Re axis so that Re(2) is hidden by Re(1). Re(2)-ligand bonds are shown with broken lines for clarity.

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Table I. Summary of Crystal Data, Data Collection Parameters, and Refinement Residuals for $Re_2Cl_3(Ph_2Ppy)_2[(C_6H_5)(C_6H_4)Ppy]$

formula	$Re_2Cl_3P_3N_3C_{51}H_{41}$	data collection instrument	Syntex $P\bar{1}$
form wt	1267.60	radiation	Mo Kα (λ_α 0.710 73 Å); graphite monochromated
space group	$P2_1/n$	scan method	ω-2θ
a, Å	12.160 (6)	data collection range, deg	$5 \leqslant 2\theta \leqslant 50$
b, Å	21.418 (7)	no. of unique data, $F_o^2 \geqslant 3\sigma(F_o^2)$	1956
c, Å	18.464 (2)	no. of parameters refined	289
β, deg	99.04 (3)	R^a	0.0502
V, Å^3	4749 (5)	$R_w{}^b$	0.0597
Z	4	quality-of-fit indicator^c	1.061
d_{calcd}, g/cm^3	1.773	largest shift/esd, final cycle	0.26
cryst size, mm	0.02 × 0.12 × 0.13 mm		
μ(Mo Kα), cm^{-1}	54.7		

[a] $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit $= [\Sigma w(|F_o| - |F_c|)^2 / (N_{obsd} - N_{parameters})]^{1/2}$.

development of new reaction chemistry associated with dinuclear complexes containing multiple bonds.

The reaction between quadruply bonded $Re_2Cl_6(P\text{-}n\text{-}Bu_3)_2$[6] and Ph_2Ppy (1:6 mole proportions) in refluxing methanol leads to the separation of red-purple crystals of **1** in 34% yield.[10a] Spectroscopic information on **1** did not resolve the question of its structure, so recourse was had to X-ray crystallography[10b] (see Table I).

The essential features of the structure are shown in Figure 1, which is a view directly down the Re–Re axis. The Re–Re bond length is 2.336 (2) Å, and there is an axial Cl atom on each rhenium atom with Re–Cl bonds, 2.573 [7] Å, that deviate by 13–18° from colinearity with the Re–Re bond. Two of the Ph_2Ppy ligands, containing P(2), N(2) and P(3), N(3), are bridging bidentate ligands of essentially the expected sort. The third one, however, is tridentate with P(1) bonded to Re(1), N(1) bonded to Re(2), and an Re(2)–C(12) bond, 2.16 (3) Å, formed by ortho metalation of one phenyl ring on P(1). The three Re–P bonds have similar lengths, 2.388 (9), 2.359 (10), and 2.354 (9) Å, for P(1), P(2), and P(3), respectively. Since the Re–Re bond is only a triple bond, there is no barrier to rotation, and it is this factor that makes the relatively unstrained[10c] three-point attachment of the ortho-metalated ligand feasible, as is evident from Figure 1.

This structure allows the interpretation of the complex NMR spectra of **1**. The ^1H NMR ($CDCl_3$) has a complex pattern in the phenyl region, while the $^{31}P\{^1H\}$ spectrum (recorded in 1:1 $CH_2Cl_2/CDCl_3$)[11] displays three resonances (each a doublet of doublets) at δ −25.81, −0.88, and +14.66; the resonance at δ −25.81 may be assigned to P(1) of the ortho-metalated ligand since this should be the most shielded.[12] The resonance at δ −0.88 is assigned to P(2), which is cis to P(1), and P(3) on the adjacent metal center to the resonance at δ +14.66, on the basis of coupling constant considerations. It would be expected that the largest coupling would occur between the cis-phosphorus atoms, which makes $^2J_{P_1-P_2} = 16.3$ Hz, and thus the smallest would be the three-bond coupling constants, $J_{P_1-P_3} = 9.3$ Hz and $^3J_{P_2-P_3} = 6.9$ Hz.[13,14]

The electrochemical properties of this complex are fully in accord with it being a derivative of Re_2^{4+}.[15,16] A cyclic voltammogram of a solution in 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH)–dichloromethane is characterized by two quasi-reversible couples at $E_{1/2} = +0.24$ and $+1.06$ V vs. SCE (using a Pt bead electrode), each of which corresponds to an oxidation. This behavior is characteristic of phosphine derivatives of this triply bonded core.[15,16]

The facile reduction of the Re_2^{6+} core by Ph_2Ppy is further demonstrated by its reactions with $Re_2Cl_6(PR_3)_2$ (R = Et or *n*-Bu) in acetone, leading, in each instance, to dark purple crystalline $Re_2Cl_4(Ph_2Ppy)_2(PR_3)$ (R = Et, **2a**, or R = *n*-Bu, **2b**).[17,18] Another reaction of note is the formation of $Re_2Cl_4(Ph_2Ppy)_3$ (**3**)[18] in 68% yield from the reaction between $(Bu_4N)_2Re_2Cl_8$ and Ph_2Ppy (1:4 mole proportions) in methanol. Changing the proportion of reagents in the latter reaction to 1:6 leads to the formation of **1** in low yield, implying that the reduced but not ortho-metalated complex **3** may be a precursor to **1**. Indeed, this has been confirmed by reacting **3** with 2 equiv of Ph_2Ppy in refluxing methanol, whereby **1** is formed in good yield.[20] Thus Ph_2Ppy not only serves to stabilize these dinuclear rhenium complexes through the formation of stable bidentate ligand bridges but, additionally, reduces the Re_2^{6+} core to Re_2^{4+} and is the base that assists in the elimination of HCl (i.e., **3** → **1**) in the ortho-metalation step. Further studies are underway to elucidate the mechanisms of these reactions and to complete the detailed structural characterization of **2a** and **3**.

Acknowledgment. Support from the National Science Foundation (Grant CHE 82-06117 to R.A.W. and Grant CHE 77-00448 to F.A.C.) is gratefully acknowledged. The Varian XL-200 spectrometer was purchased with funds from the National Science Foundation (Grant CHE 80-04246 to Purdue). This support is gratefully acknowledged.

Registry No. 1, 85665-22-1; Ph_2Ppy, 85665-23-2; **2b**, 85665-24-3; **3**, 85650-36-8; $Re_2Cl_6(P\text{-}n\text{-}Bu_3)_2$, 38832-70-1; Ph_2Ppy, 37943-90-1; $Re_2Cl_6(PEt_3)_2$, 19584-31-7; $(Bu_4N)_2Re_2Cl_8$, 14023-10-0.

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(10) (a) Anal. Calcd for $C_{51}H_{41}Cl_3N_3P_3Re_2$: C, 48.32; H, 3.26; Cl, 8.39. Found: C, 47.78; H, 3.33; Cl, 8.64. (b) **1** crystallizes in space group $P2_1/n$ with unit-cell dimensions a = 12.160 (6) Å, b = 21.418 (7) Å, c = 18.464 (2) Å, β = 99.04 (3)°, and Z = 4. No crystallographic symmetry is imposed on the molecule. Using 1956 unique data with $I > 3\sigma(I)$, collected at room temperature from 5 to 50° in 2θ, 289 parameters were refined to R_1 = 0.0502, R_2 = 0.0597, and a quality-of-fit indicator of 1.061. (c) There are some slightly abnormal angles at P(1), viz., Re(1)–P(1)–C(21): 127 (1)° and C(1A)–P(1)–C(11): 97 (1)°. The other four are in the range 105–111°.

(11) $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-200 spectrometer operated at 80.98 MHz with an internal deuterium lock and aqueous 85% H_3PO_4 as an external standard. Positive chemical shifts were measured downfield from H_3PO_4.

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(13) Other spectroscopic properties of note include its IR spectrum with ν(Re–Cl) at 298s cm^{-1} and an absorption band at 1560 mw cm^{-1}, which may be characteristic of the ortho-metalated phenyl ring, as observed in the IR spectra of other ortho-metalated complexes.[14]

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(17) The structure of **2a** has been determined by X-ray crystallography. It is dinuclear with Re–Re = 2.270 (1) Å, and two cis, oppositely directed bridging Ph_2Ppy ligands. One Re atom also has two cis equatorial Cl ligands while the other has cis Cl and PEt_3 ligands and a weakly coordinated axial Cl ligand.

(18) The $^{31}P\{^1H\}$ NMR (CH_2Cl_2–$CDCl_3$) of these complexes (three doublets of doublets) were in all instances consistent with the presence of three inequivalent phosphorus environments. **2a**: δ −25.48, −7.24, +13.68. **2b**: −29.71, −8.31, +13.73. **3**: δ −6.50, −5.45, −0.37. The magnitudes of the observed coupling constants (11.1–3.9 Hz) would seem to preclude the presence of any *trans*-(P–Re–P) units.[19] Full spectral details will be published at a later date.

(19) Reference 12, p 32.

(20) The conversion of **3** to **1** can be followed conveniently by using the CV technique. Both complexes exhibit two one-electron oxidations in 0.2 M TBAH–dichloromethane ($E_{1/2}$ = +0.24 and +1.06 V for **1** and $E_{1/2}$ = 0.41 and +1.20 V for **3** vs. SCE). Additional experiments show that other bases (e.g., $Ph_2PCH_2PPh_2$ and $Ph_2PNHPPh_2$) bring about this same conversion (as monitored by CV).