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Contribution from the Department of Chemistry,
University of California, Davis, California 95616

Preparation of Binuclear Complexes Using 2-(Diphenylphosphino)pyridine as a Bridging Ligand. Synthesis of Some Ruthenium Complexes and Their Interaction with Palladium Complexes

ANDRE MAISONNET, JAMES P. FARR, MARILYN M. OLMSTEAD, CATHERINE T. HUNT, and ALAN L. BALCH*

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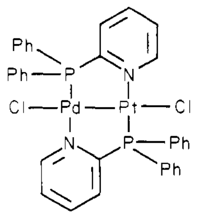
The reactions between $\mathrm{Ru(Ph_2Ppy)_2(CO)_3}$ and (1,5-cyclooctadiene)$\mathrm{PdCl_2}$ and between $\mathrm{Ru(Ph_2Ppy)_2(CO)_2Cl_2}$ and $\mathrm{Pd_2}$(dibenzylideneacetone)$_3$ have been examined as routes to binuclear Ru/Pd complexes. The first reaction produces $\mathrm{Ru(Ph_2Ppy)_2(CO)_2Cl_2}$, $\mathrm{Ru(Ph_2Ppy)(CO)_2Cl_2}$, $\mathrm{Pd_2(Ph_2Ppy)_2Cl_2}$, and two isomers of $\mathrm{RuPd(Ph_2Ppy)_2(CO)_2Cl_2}$, while the second forms predominantly the two binuclear products. Syntheses of $\mathrm{Ru_3(CO)_9(Ph_2Ppy)_3}$, $\mathrm{Ru(Ph_2Ppy)_2(CO)_3}$, and $\mathrm{Ru(Ph_2Ppy)_2(CO)_2Cl_2}$ from $\mathrm{Ru_3(CO)_{12}}$ are reported as are the preparations of $\mathrm{Pd(Ph_2Ppy)_2Cl_2}$ and $\mathrm{Pd_2(Ph_2Ppy)_2Cl_2}$. All new compounds have been characterized by infrared spectroscopy and $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectroscopy. The two isomers of $\mathrm{RuPd(Ph_2Ppy)_2(CO)_2Cl_2}$ interconvert on heating in solution. The structure of one isomer has been determined unambiguously by X-ray crystallography. $\mathrm{RuPd(Ph_2Ppy)_2(CO)_2Cl_2}$ crystallizes in the space group $P2_1/c$ with cell dimensions (determined at 140 K) of $a = 10.493$ (2) Å, $b = 17.685$ (4) Å, $c = 21.470$ (5) Å, $\beta = 92.07$ (2)°, $Z = 4$, and $V = 3982$ (1) Å^3. The structure was refined by blocked cascade least-squares to a conventional R value of 0.043 by using 4605 significant reflections. The compound possesses a Pd–Ru bond with a distance of 2.660 (1) Å. The palladium atom is four-coordinate with a Ru, Cl, P, N donor set, while the ruthenium atom is six-coordinate with a Pd, Cl, P, N, $\mathrm{C_2}$ donor set.

Introduction

The ligand 2-(diphenylphosphino)pyridine ($\mathrm{Ph_2Ppy}$) has been used to prepare bridged heterobinuclear transition-metal complexes in high yield.[1-4] The basic reaction pattern we have employed has involved sequential binding of the ligand to the first metal by the phosphorus atom followed by complexation to the second metal atom. Some representative reactions that demonstrate the second step are given in eq 1–3.

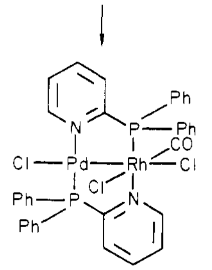
Here we report our results on using $\mathrm{Ph_2Ppy}$ to form some ruthenium complexes. We undertook this work for two reasons. Although there has been extensive study of binuclear, phosphine-bridged complexes of many of the group 8 elements,[5-12] little has been done with either ruthenium or osmium. For example, bis(diphenylphosphino)methane forms a host of well-characterized binuclear complexes with platinum, palladium, nickel, iridium, rhodium, cobalt, and iron, but with ruthenium its only known compounds are trinuclear substitution products of $\mathrm{Ru_3(CO)_{12}}$[13-15] and chelated ruthenium(II) complexes.[16] Secondly, complexes of ruthenium in its lower oxidation states tend to be coordinatively saturated. We know that this would inhibit access to the metal, and hence it would slow down the reactions analogous to those given in eq 1–3. Thus it remained to be seen whether any binuclear complexes could be assembled in this fashion.

$\mathrm{Pd(Ph_2Ppy)_2Cl_2}$ + $\mathrm{Pt(dba)_2}$ ⟶
(dba = dibenzylideneacetone)



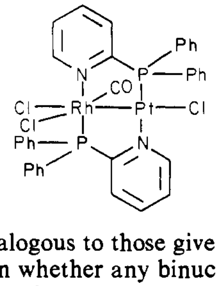
1 (1)

trans-$\mathrm{Rh(CO)Cl(Ph_2Ppy)_2}$ + (1,5-COD)$\mathrm{PdCl_2}$
(1,5-COD = 1,5-cyclooctadiene)



2 (2)

cis-$\mathrm{Pt(Ph_2Ppy)_2Cl_2}$ + $\frac{1}{2}\mathrm{Rh_2(\mu\text{-}Cl)_2(CO)_4}$ ⟶



(3)

Results and Discussion

Synthesis of Monomeric Ruthenium Complexes. The syntheses of a variety of ruthenium complexes of $\mathrm{Ph_2Ppy}$ are summarized in Scheme I. Beginning with $\mathrm{Ru_3(CO)_{12}}$, we have obtained the monomers $\mathrm{Ru(Ph_2Ppy)_3(CO)_3}$, $\mathrm{Ru(Ph_2Ppy)_2(CO)_2Cl_2}$, and $\mathrm{Ru(Ph_2Ppy)(CO)_2Cl_2}$, as well as trinuclear

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(1) Farr, J. P.; Olmstead, M. M.; Balch, A. L. *A. Am. Chem. Soc.* **1980**, *101*, 6654–6656.
(2) Farr, J. P.; Olmstead, M. M.; Hunt, C. H.; Balch, A. L. *Inorg. Chem.* **1981**, *20*, 1182–1187.
(3) Maisonnat, A.; Farr, J. P.; Balch, A. L. *Inorg. Chim. Acta* **1981**, *53*, L217–L218.
(4) Farr, J. P.; Olmstead, M. M.; Wood, F.; Balch, A. L., submitted for publication.
(5) Balch, A. L. In "Homogeneous Catalysis with Metal Phosphine Complexes"; Pignolet, L. H., Ed.; Plenum Press: New York, in press.
(6) Balch, A. L. In "Reactivity of Metal-Metal Bonds"; Chisholm, M. H., Ed.; American Chemical Society: Washington, D.C., 1981; ACS Symp. Ser. No. 155, pp 167–186.
(7) Puddephatt, R. J. In "Reactivity of Metal–Metal Bonds"; Chisholm, M. H., Ed.; American Chemical Society: Washington, D.C., 1981; ACS Symp. Ser. No. 155, pp 187–196.
(8) Balch, A. L. In "Catalytic Aspects of Metal Phosphine Complexes"; Alyea, E. C., Meek, D. W., Eds.; American Chemical Society: Washington, D.C.; ACS Symp. Ser., in press.
(9) Kubiak, C. P.; Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1980**, *19*, 2733–2739.
(10) Cowie, M.; Dickson, R. S. *Inorg. Chem.* **1981**, *20*, 2682–2688.
(11) Mague, J. T.; Sanger, A. R. *Inorg. Chem.* **1979**, *18*, 2060–2066.
(12) Hoffmann, D. M.; Hoffmann, R. *Inorg. Chem.* **1981**, *20*, 3543–3555.
(13) Cotton, F. A.; Hanson, B. E. *Inorg. Chem.* **1977**, *16*, 3369–3371.
(14) Lavigne, G.; Bonnet, J.-J. *Inorg. Chem.* **1981**, *20*, 2713–2716.
(15) Lavigne, G.; Lugan, N.; Bonnet, J.-J. *Nouv. J. Chim.* **1981**, *5*, 423–425.
(16) Mague, J. T.; Mitchener, J. P. *Inorg. Chem.* **1972**, *11*, 2714–2720.

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Scheme I

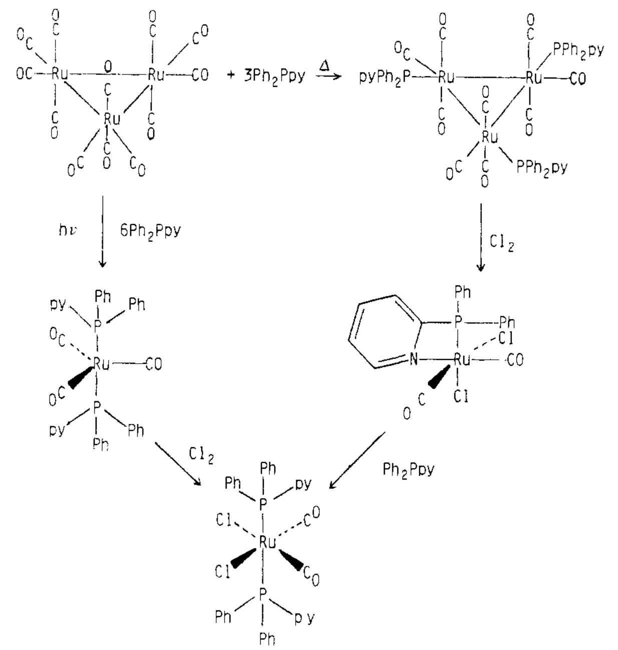

Table I. Spectroscopic Parameters for Ruthenium and Palladium Compounds

compd	$^{31}P\{^1H\}$ NMR,^{a} δ (*J*, Hz)	ν(C≡O),^{a} cm^{-1}
$Ru_3(CO)_9(Ph_2Ppy)_3$	37.7	2045 vw, 1975 vs
$Ru_3(CO)_9(PPh_3)_3$		2044 vs, 1978 sh, 1967 s, br
$Ru(Ph_2Ppy)_2(CO)_3$	57.8	1895 vs
$Ru(PPh_3)_2(CO)_3$	55.7	1895 vs
$Ru(Ph_2Ppy)(CO)_2Cl_2$	−6.8	2067 vs, 2007 vs
$Ru(Ph_2Ppy)_2(CO)_2Cl_2$	21.5	2062 vs, 2001 vs
$Ru(PPh_3)_2(CO)_2Cl_2$	17.8	2058 vs, 1996 vs
$Pd(Ph_2Ppy)_2Cl_2$	23.8, 29.3^b	none
$Pd_2(Ph_2Ppy)_2Cl_2$	4.4	none
$RuPd(Ph_2Ppy)_2(CO)_2Cl_2$, D	38.9 d (7.5), 17.9 d (7.5)	2013 vs, 1954 vs
$RuPd(Ph_2Ppy)_2(CO)_2Cl_2$, E	20.1 d (2), 16.5 d (2)	2025 vs, 1965 vs

^{a} In dichloromethane solution. ^{b} Two singlets with an intensity ratio of 1:1.9 are observed. These are believed to arise from the presence of cis and trans isomers.

$Ru_3(Ph_2Ppy)_3(CO)_9$. Analogues of all of these, with the exception of $Ru(Ph_2Ppy)(CO)_2Cl_2$, have been made earlier with triphenylphosphine. Our synthetic procedures have been based upon the routes developed to the triphenylphosphine analogues.[17-20] The $^{31}P\{^1H\}$ NMR and infrared spectroscopic data in Table I reveal very close similarities between the two series of materials. Consequently the structures of the two series of compounds can be taken to be similar, and our structural assignments follow those previously made for the triphenylphosphine analogues.

The one unique compound is $Ru(Ph_2Ppy)(CO)_2Cl_2$. This has no triphenylphosphine analogue because the phosphine ligand here is bonding as a chelate rather than as a monodentate ligand. The geometric details of its structure have been determined from an X-ray crystallographic study that verifies the presence of the somewhat strained four-membered chelate ring.[21] This chelated complex is most readily synthesized by the chlorination of $Ru_3(CO)_9(Ph_2Ppy)_3$ as reported earlier.[21]

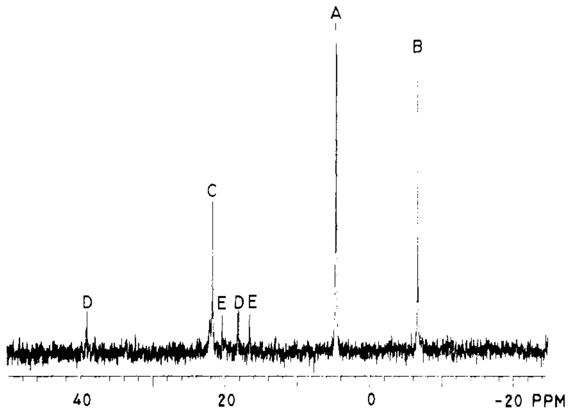

Figure 1. $^{31}P\{^1H\}$ NMR spectrum of a dichloromethane solution prepared from a 1:1 molar ratio of $Ru(Ph_2Ppy)_2(CO)_3$ and (1,5-COD)$PdCl_2$. Compounds present have been identified as follows: A, $Pd_2(Ph_2Ppy)_2Cl_2$; B, $Ru(Ph_2Ppy)(CO)_2Cl_2$; C, $Ru(Ph_2Ppy)_2(CO)_2Cl_2$; D and E, isomers of $RuPd(Ph_2Ppy)_2(CO)_2Cl_2$.

Reaction between $Ru(Ph_2Ppy)_2(CO)_3$ and (1,5-COD)$PdCl_2$. The first attempt to construct a heterobinuclear or Ru/Pd complex involved the interaction of $Ru(Ph_2Ppy)_2(CO)_3$ and (1,5-COD)$PdCl_2$. We felt this would be analogous to the reaction between $Rh(Ph_2Ppy)_2(CO)Cl$ and (1,5-COD)$PdCl_2$, which produced $RhPd(Ph_2Ppy)_2(CO)Cl_3$, eq 2. The $^{31}P\{^1H\}$ NMR spectrum of the products of the reaction in dichloromethane recorded after a reaction time of 5 min is shown in Figure 1. At least five species, labeled A–E, are present in the deep red-brown solution. Three of these produce singlets in the spectrum while the other two give rise to pairs of doublets with small coupling constants (D, 7.5 Hz; E, 2 Hz), which can only be ascribed to phosphorus–phosphorus coupling.

By a process of fractional crystallization and independent synthesis it has been possible to identify the products as follows: A, $Pd_2(Ph_2Ppy)_2Cl_2$; B, $Ru(PPh_2Ppy)(CO)_2Cl_2$; C, $Ru(Ph_2Ppy)_2(CO)_2Cl_2$; D and E, isomers of composition $RuPd(Ph_2Ppy)_2(CO)_2Cl_2$. They are formed in the following yields (%): A, 38; B, 31; C, 16; D, 8; E, 7. The identification of these components is described in succeeding sections.

Reaction of $Ru(Ph_3P)_2(CO)_3$ with (1,5-COD)$PdCl_2$. This reaction was run for comparison with the previous reaction under identical conditions. The reaction rapidly produced a black precipitate of palladium metal, which was removed by filtration. Analysis of the remaining solution by $^{31}P\{^1H\}$ NMR spectroscopy and by infrared spectroscopy showed that $Ru(PPh_3)_2(CO)_2Cl_2$ had formed in 78% yield. Thus the predominant reaction is as given in eq 4. As a result of this

$$Ru(Ph_3P)_2(CO)_3 + (1,5\text{-COD})PdCl_2 \rightarrow Ru(Ph_3P)_2(CO)_2Cl_2 + 1,5\text{-COD} + Pd + CO \quad (4)$$

comparison, we can ascribe the formation of $Ru(Ph_2Ppy)_2(CO)_2Cl_2$ in the preceding section to a natural redox process between Ru(0) and Pd(II), which does not require the presence of the bifunctional phosphinopyridine ligand.

Formation and Attempted Formation of Homobinuclear Compounds. Compound A, the species responsible for the red-brown color that develops when $Ru(Ph_2Ppy)_2(CO)_3$ reacts with (1,5-COD)$PdCl_2$, was found to be the Pd(I) complex $Pd_2(Ph_2Ppy)_2Cl_2$ (**4**). This species is isoelectronic with the well-studied $Pd_2(dpm)_2Cl_2$ but lacks the reactivity associated

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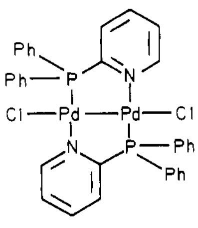
(17) Piacenti, F.; Bianchi, M.; Benedetti, E.; Braca, G. *Inorg. Chem.* **1968**, *7*, 1815–1817.

(18) Johnson, B. F. G.; Twig, M. V. *J. Organomet. Chem.* **1974**, *67*, C75–C76.

(19) Bruce, M. I.; Shaw, G.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1972**, 2094–2099.

(20) Collman, J. P.; Roper, R. W. *J. Am. Chem. Soc.* **1965**, *87*, 4008–4009.

(21) Olmstead, M. M.; Maisonnat, A.; Farr, J. P.; Balch, A. L. *Inorg. Chem.* **1981**, *20*, 4060–4064.



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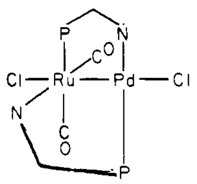
with the Pd–Pd bond of the latter complex.[22] $Pd_2(Ph_2Ppy)_2Cl_2$ has been independently prepared by the conproportionation reaction between Pd(II) and Pd(0) compounds, which is a generally useful method for the preparation of dimeric Pd(I) complexes.[22,23] Thus treatment of $Pd(Ph_2Ppy)_2Cl_2$, which was made from $(PhCN)_2PdCl_2$ and Ph_2Ppy, with $Pd_2(dba)_3$ in dichloromethane solution produces $Pd_2(Ph_2Ppy)_2Cl_2$ in 90% yield. While the spectroscopic data do not distinguish between head-to-tail and head-to-head orientations of the Ph_2Ppy ligands, the head-to-tail structure, **4**, is more likely since the heteronuclear $PtPd(Ph_2Ppy)_2Cl_2$ has been shown to have this structure.[3]

Because of the facile formation of a number of homonuclear dimers (including dimers of Pd(I), Pt(I), and Rh(II)) by this type of conproportionation reaction,[22-26] conproportionation reactions between Ru(0) and Ru(II) compounds were examined. No reaction occurs in mixtures of $Ru(Ph_2Ppy)_2(CO)_3$ and $Ru(Ph_2Ppy)_2(CO)_2Cl_2$ or of $Ru(Ph_3P)_2(CO)_3$ and $Ru(Ph_3P)_2(CO)_2Cl_2$ in dichloromethane solution after 2 days, a much longer time than required for any of the other reactions reported here.

Reaction between $Ru(Ph_2Ppy)_2(CO)_2Cl_2$ and Pd(0). By reversing the oxidation states of ruthenium and palladium in the reaction between their complexes, it is possible to alter the product distribution so that the binuclear complexes become the predominant products. Thus the reaction between $Ru(Ph_2Ppy)_2(CO)_2Cl_2$ and the palladium(0) olefin complex $Pd_2(dba)_3$[27] yields the same compounds, D and E, as formed from the reaction of $Ru(Ph_2Ppy)_2(CO)_3$ with $(1,5\text{-COD})PdCl_2$. These two compounds may be separated by either fractional crystallization or chromatography on silica gel.

Compounds D and E are isomers of composition $RuPd(Ph_2Ppy)_2(CO)_2Cl_2$. Both compounds have similar infrared spectra and therefore similar structural elements. The infrared spectrum of each isomer is consistent with the presence of two cis-carbonyl groups. The $^{31}P\{^1H\}$ NMR spectra of D and E indicate that in each there are two inequivalent phosphine ligands. These cannot lie trans to one another and be bonded to the same metal. This condition would produce P–P coupling constants much larger than the observed values. Consequently compounds D and E may have any of the isomeric structures **5**–**7**, if both phosphine ligands are bridging. If only one phosphine ligand is bridging, there are 13 other structures that are consistent with the data (with the constraint of a cis $Ru(CO)_2$ unit), but we feel this situation is much less likely.



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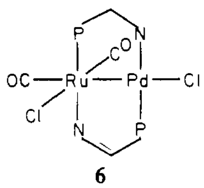

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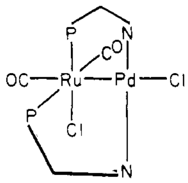

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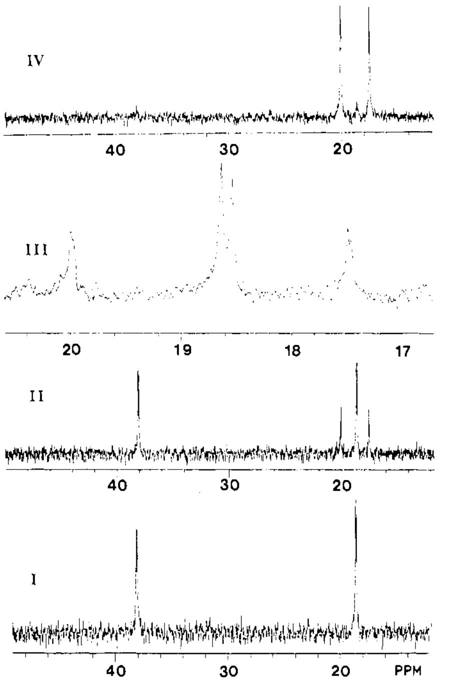

Figure 2. $^{31}P\{^1H\}$ NMR (chloroform solutions): (I) spectrum of $RuPd(Ppy)_2(CO)_2Cl_2$, isomer D; (II) spectrum of the same solution as shown in part I after heating to 60 °C for 20 min, showing isomerization D → E; (III) expanded version of part of spectrum II, showing the doublet nature of the spectrum of E; (IV) spectrum of $RuPd(Ph_2Ppy)_2(CO)_2Cl_2$, isomer E.

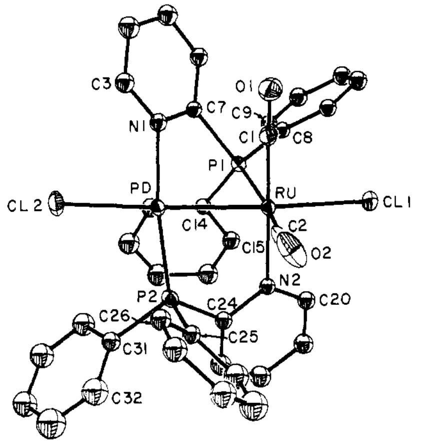

Figure 3. Perspective drawing of the molecular structure of $RuPd(Ph_2Ppy)_2(CO)_2Cl_2$, isomer E.

The isomeric compounds D and E can be interconverted thermally. This is shown in Figure 2, which presents in traces I and IV the spectra of D and E, respectively. When a sample of D is heated in chloroform solution to 60 °C, it isomerizes partially to E as shown in trace II. Similarly pure E is converted into a mixture of D and E upon heating. Since this is a reversible conversion (regardless of whether we start with D or E the same mixture results), the equilibrium constant for reaction 5 can be estimated. From integration of the ^{31}P NMR spectra, K_{eq} is 2.5 for reaction 5 in chloroform solution.

$$D \rightleftharpoons E \qquad (5)$$

Crystal and Molecular Structure of E, $RuPd(Ph_2Ppy)_2(CO)_2Cl_2$. So that the details of the structure of the two binuclear isomers D and E could be determined, attempts were made to obtain suitable samples for X-ray crystallography.

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(22) Benner, L. S.; Balch, A. L. *J. Am. Chem. Soc.* **1978**, *100*, 6099–6106.

(23) Boehm, J. R.; Doonan, D. J.; Balch, A. L. *J. Am. Chem. Soc.* **1976**, *98*, 4845–4850.

(24) Balch, A. L. *Ann. N.Y. Acad. Sci.* **1978**, *313*, 651–662.

(25) Balch, A. L.; Olmstead, M. M. *J. Am. Chem. Soc.* **1976**, *98*, 2354–2356.

(26) Olmstead, M. M.; Balch, A. L. *J. Organomet. Chem.* **1978**, *148*, C15–C18.

(27) Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnett, J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253–266.

Table II. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) for $RuPd(Ph_2Ppy)_2(CO)_2Cl_2$

atom	*x*	*y*	*z*	*U*
Ru	3808.0 (4)	−72.2 (3)	1859.9 (2)	14.3 (2)[a]
Pd	2417.4 (4)	1185.6 (3)	1841.0 (2)	16.0 (2)[a]
Cl(1)	5015 (2)	−1271.4 (9)	1793.4 (7)	22.8 (5)[a]
Cl(2)	1345 (2)	2400.9 (9)	1814.8 (8)	32.6 (6)[a]
Cl(3)	5326 (2)	2281 (1)	1777 (1)	51.2 (7)[a]
Cl(4)	4906 (3)	3539 (1)	938 (1)	72 (1)[a]
P(1)	2198 (2)	−265.9 (9)	1055.6 (7)	16.4 (5)[a]
P(2)	2188 (2)	894.6 (9)	2822.2 (8)	18.5 (5)[a]
N(1)	2497 (5)	1219 (3)	853 (2)	19 (1)
N(2)	2591 (5)	−566 (3)	2553 (2)	17 (1)
O(1)	5462 (4)	598 (3)	893 (2)	35 (2)[a]
O(2)	5924 (5)	513 (3)	2724 (3)	47 (2)[a]
C(1)	4803 (6)	351 (4)	1263 (3)	21 (2)[a]
C(2)	5075 (6)	290 (4)	2446 (3)	26 (2)[a]
C(3)	2719 (6)	1846 (4)	533 (3)	23 (1)
C(4)	2855 (6)	1843 (4)	−106 (3)	29 (2)
C(5)	2734 (6)	1172 (4)	−427 (3)	27 (2)
C(6)	2432 (6)	515 (4)	−104 (3)	22 (1)
C(7)	2329 (6)	559 (3)	543 (3)	17 (1)
C(8)	2237 (6)	−1052 (3)	499 (3)	18 (1)
C(9)	1141 (6)	−1293 (4)	175 (3)	21 (1)
C(10)	1214 (6)	−1843 (4)	−272 (3)	26 (2)
C(11)	2384 (6)	−2163 (4)	−401 (3)	26 (2)
C(12)	3465 (6)	−1930 (4)	−86 (3)	25 (2)
C(13)	3405 (6)	−1370 (4)	365 (3)	20 (1)
C(14)	570 (6)	−299 (4)	1324 (3)	18 (1)
C(15)	178 (6)	−964 (4)	1602 (3)	23 (1)
C(16)	−996 (7)	−1009 (4)	1878 (3)	31 (2)
C(17)	−1778 (7)	−385 (4)	1865 (3)	37 (2)
C(18)	−1427 (7)	269 (4)	1583 (3)	34 (2)
C(19)	−236 (6)	323 (4)	1310 (3)	25 (2)
C(20)	2452 (6)	−1326 (4)	2613 (3)	21 (1)
C(21)	1616 (6)	−1643 (4)	3006 (3)	27 (2)
C(22)	851 (7)	−1181 (4)	3360 (3)	31 (2)
C(23)	1002 (7)	−413 (4)	3308 (3)	29 (2)
C(24)	1863 (6)	−120 (4)	2916 (3)	19 (1)
C(25)	3487 (6)	1060 (4)	3393 (3)	18 (1)
C(26)	4093 (6)	1759 (4)	3384 (3)	22 (1)
C(27)	5057 (6)	1913 (4)	3811 (3)	28 (2)
C(28)	5461 (7)	1384 (4)	4244 (3)	33 (2)
C(29)	4866 (7)	682 (5)	4241 (4)	42 (2)
C(30)	3868 (7)	522 (4)	3826 (3)	34 (2)
C(31)	835 (6)	1335 (4)	3201 (3)	21 (1)
C(32)	933 (8)	1605 (4)	3797 (4)	42 (2)
C(33)	−107 (8)	1928 (5)	4077 (4)	53 (2)
C(34)	−1251 (7)	1989 (4)	3759 (4)	39 (2)
C(35)	−1369 (7)	1708 (4)	3158 (4)	38 (2)
C(36)	−327 (7)	1387 (4)	2872 (3)	33 (2)
C(37)	4550 (8)	3151 (5)	1669 (4)	47 (3)[a]
C(38)	−1871 (30)	−18 (17)	4429 (15)	38 (7)
Cl(5)	−1939 (7)	526 (4)	5106 (3)	36 (2)
Cl(6)	−1687 (9)	−847 (6)	4426 (4)	59 (2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U tensor.

Only compound E gave satisfactory results. Attempts to crystallize D slowly always produced crystals of E along with unsuitable crystals of D.

$RuPd(Ph_2Ppy)_2(CO)_2Cl_2$, isomer E, crystallizes with one molecule in the asymmetric unit. A perspective drawing with the atom numbering scheme is given in Figure 3. A stereoscopic view of the molecule is shown in Figure 4 (supplementary material). As can be seen from these views, the molecule possesses no symmetry and corresponds to isomeric structure **5**. Atomic coordinates and temperature factors are given in Table II. Selected interatomic distances and angles are presented in Tables III and IV.

Table III. Bond Lengths (Å) in $RuPd(Ph_2Ppy)_2(CO)_2Cl_2$

Ru–Pd	2.660 (1)	Ru–Cl(1)	2.477 (2)
Ru–P(1)	2.396 (2)	Ru–N(2)	2.178 (5)
Ru–C(1)	1.841 (7)	Ru–C(2)	1.908 (7)
Pd–Cl(2)	2.426 (2)	Pd–P(2)	2.190 (2)
Pd–N(1)	2.126 (5)	Cl(3)–C(37)	1.753 (9)
Cl(4)–C(37)	1.764 (8)	P(1)–C(7)	1.836 (6)
P(1)–C(8)	1.834 (6)	P(1)–C(14)	1.824 (6)
P(2)–C(24)	1.838 (6)	P(2)–C(25)	1.824 (6)
P(2)–C(31)	1.835 (7)	N(1)–C(3)	1.330 (8)
N(1)–C(7)	1.353 (8)	N(2)–C(20)	1.357 (8)
N(2)–C(24)	1.364 (8)	O(1)–C(1)	1.157 (8)
O(2)–C(2)	1.127 (9)	C(3)–C(4)	1.383 (9)
C(4)–C(5)	1.38 (1)	C(5)–C(6)	1.397 (9)
C(6)–C(7)	1.398 (9)	C(8)–C(9)	1.390 (9)
C(8)–C(13)	1.388 (9)	C(9)–C(10)	1.371 (9)
C(10)–C(11)	1.389 (9)	C(11)–C(12)	1.364 (9)
C(12)–C(13)	1.387 (9)	C(14)–C(15)	1.387 (9)
C(14)–C(19)	1.388 (9)	C(15)–C(16)	1.39 (1)
C(16)–C(17)	1.37 (1)	C(17)–C(18)	1.36 (1)
C(18)–C(19)	1.40 (1)	C(20)–C(21)	1.361 (9)
C(21)–C(22)	1.39 (1)	C(22)–C(23)	1.37 (1)
C(23)–C(24)	1.360 (9)	C(25)–C(26)	1.390 (9)
C(25)–C(30)	1.379 (9)	C(26)–C(27)	1.367 (9)
C(27)–C(28)	1.37 (1)	C(28)–C(29)	1.39 (1)
C(29)–C(30)	1.38 (1)	C(31)–C(32)	1.37 (1)
C(31)–C(36)	1.390 (9)	C(32)–C(33)	1.39 (1)
C(33)–C(34)	1.36 (1)	C(34)–C(35)	1.38 (1)
C(35)–C(36)	1.39 (1)	C(38)–Cl(5)	1.75 (3)
C(38)–Cl(6)	1.48 (3)		

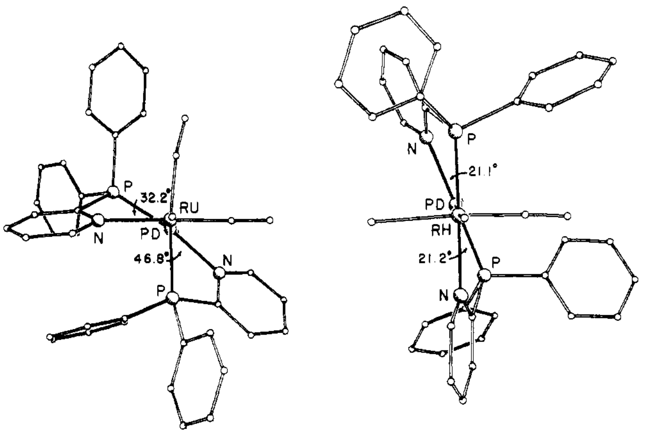
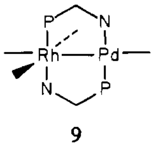


Figure 5. Projections down the Cl–Ru and Cl–Rh bonds of $RuPd(Ph_2Ppy)_2(CO)_2Cl_2$ and $RhPd(Ph_2Ppy)_2(CO)Cl_3$ showing the N–M–M′–P dihedral angles.

The palladium atom is four-coordinate with nearly planar coordination while the ruthenium is six-coordinate. The two metal atoms are joined by a metal–metal bond whose length (2.660 (1) Å) is consistent with the presence of a Ru–Pd single bond. In electron-counting terms the ruthenium may be considered as Ru(I) and the palladium as Pd(I), with the ruthenium atom being a coordinatively saturated, 18-electron center while the palladium is a coordinatively unsaturated, 16-electron center.

The structure of $RuPd(Ph_2Ppy)_2(CO)_2Cl_2$ may be compared to that of $RhPd(Ph_2Ppy)_2(CO)Cl_3$ (**12**).[1] The latter contains a four-coordinate, planar palladium atom and a six-coordinate rhodium atom. The two are joined by a Rh–Pd single bond. The metal–metal bond lengths in the two complexes are similar: Ru–Pd, 2.660 (1) Å; Rh–Pd, 2.594 (1) Å. A major difference between the two involves the relative orientation of the two bridging diphosphine ligands. In $RhPd(Ph_2Ppy)_2(CO)Cl_3$ these adopt a head-to-tail arrangement and lie trans to one another on each metal as shown in **9**. This is the most common geometric orientation that is found for



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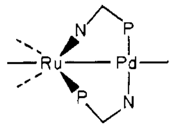

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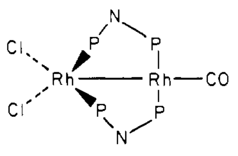
Table IV. Bond Angles (Deg) in $RuPd(Ph_2Ppy)_2(CO)_2Cl_2$

Pd–Ru–Cl(1)	175.3 (1)	Pd–Ru–P(1)	74.7 (1)
Cl(1)–Ru–P(1)	100.6 (1)	Pd–Ru–N(2)	90.6 (1)
Cl(1)–Ru–N(2)	90.5 (1)	P(1)–Ru–N(2)	91.1 (1)
Pd–Ru–C(1)	88.5 (2)	Cl(1)–Ru–C(1)	90.2 (2)
P(1)–Ru–C(1)	87.7 (2)	N(2)–Ru–C(1)	178.7 (2)
Pd–Ru–C(2)	95.6 (2)	Cl(1)–Ru–C(2)	88.9 (2)
P(1)–Ru–C(2)	168.4 (2)	N(2)–Ru–C(2)	95.5 (2)
C(1)–Ru–C(2)	85.6 (3)	Ru–Pd–Cl(2)	174.3 (1)
Ru–Pd–P(2)	82.4 (1)	Cl(2)–Pd–P(2)	99.4 (1)
Ru–Pd–N(1)	89.8 (1)	Cl(2)–Pd–N(1)	89.3 (1)
P(2)–Pd–N(1)	167.3 (1)	Ru–P(1)–C(7)	104.6 (2)
Ru–P(1)–C(8)	123.1 (2)	C(7)–P(1)–C(8)	101.9 (3)
Ru–P(1)–C(14)	114.9 (2)	C(7)–P(1)–C(14)	107.9 (3)
C(8)–P(1)–C(14)	103.0 (3)	Pd–P(2)–C(24)	111.2 (2)
Pd–P(2)–C(25)	120.2 (2)	C(24)–P(2)–C(25)	102.7 (3)
Pd–P(2)–C(31)	116.1 (2)	C(24)–P(2)–C(31)	102.5 (3)
C(25)–P(2)–C(31)	101.9 (3)	Pd–N(1)–C(3)	123.6 (4)
Pd–N(1)–C(7)	117.3 (4)	C(3)–N(1)–C(7)	119.1 (5)
Ru–N(2)–C(20)	122.0 (4)	Ru–N(2)–C(24)	120.8 (4)
C(20)–N(2)–C(24)	117.1 (5)	Ru–C(1)–O(1)	177.6 (6)
Ru–C(2)–O(2)	170.7 (6)	N(1)–C(3)–C(4)	122.5 (6)
C(3)–C(4)–C(5)	119.3 (6)	C(4)–C(5)–C(6)	119.2 (6)
C(5)–C(6)–C(7)	118.3 (6)	P(1)–C(7)–N(1)	113.6 (4)
P(1)–C(7)–C(6)	124.1 (5)	N(1)–C(7)–C(6)	121.6 (6)
P(1)–C(8)–C(9)	121.4 (6)	P(1)–C(8)–C(13)	118.9 (4)
C(9)–C(8)–C(13)	119.5 (6)	C(8)–C(9)–C(10)	120.1 (6)
C(9)–C(10)–C(11)	120.1 (6)	C(10)–C(11)–C(12)	120.2 (6)
C(11)–C(12)–C(13)	120.3 (6)	C(8)–C(13)–C(12)	119.8 (6)
C(1)–C(14)–C(15)	117.3 (5)	P(1)–C(14)–C(19)	123.0 (5)
C(15)–C(14)–C(19)	119.4 (6)	C(14)–C(14)–C(16)	121.0 (6)
C(15)–C(16)–C(17)	118.8 (7)	C(16)–C(17)–C(18)	121.4 (7)
C(17)–C(18)–C(19)	120.2 (7)	C(14)–C(19)–C(18)	119.3 (6)
N(2)–C(20)–C(21)	122.8 (6)	C(20)–C(21)–C(22)	119.6 (6)
C(21)–C(22)–C(23)	117.8 (7)	C(22)–C(23)–C(24)	120.6 (6)
P(2)–C(24)–N(2)	113.1 (4)	P(2)–C(24)–C(23)	124.8 (5)
N(2)–C(24)–C(23)	122.1 (6)	P(2)–C(25)–C(26)	117.7 (5)
P(2)–C(25)–C(30)	122.2 (5)	C(26)–C(25)–C(30)	120.1 (6)
C(25)–C(26)–C(27)	119.7 (6)	C(26)–C(27)–C(28)	121.4 (6)
C(27)–C(28)–C(29)	118.6 (7)	C(28)–C(29)–C(30)	121.0 (7)
C(25)–C(30)–C(29)	119.2 (7)	P(2)–C(31)–C(32)	122.0 (5)
P(2)–C(31)–C(36)	118.8 (5)	C(32)–C(31)–C(36)	119.2 (6)
C(31)–C(32)–C(33)	121.1 (7)	C(32)–C(33)–C(34)	120.5 (8)
C(33)–C(34)–C(35)	119.1 (8)	C(34)–C(35)–C(36)	120.7 (7)
C(31)–C(36)–C(35)	119.4 (7)	Cl(3)–C(37)–Cl(4)	110.3 (5)
Cl(5)–C(38)–Cl(6)	124 (2)		

binuclear complexes containing two bridging diphosphine ligands. In $RuPd(Ph_2Ppy)_2(CO)_2Cl_2$, however, while the ligands still have a head-to-tail arrangement and are trans to each other on the palladium atom, they are cis to each other at the ruthenium atom as shown in **10**. Thus the PRhN angle in $RhPd(Ph_2Ppy)_2(CO)Cl_3$ is 178.1 (5)° while the PRuN angle in $RuPd(Ph_2Ppy)_2(CO)_2Cl_2$, isomer E, is 91.1 (1)°. Similarly the P–M–Pd–N dihedral angles differ. This is best appreciated by referring to Figure 5, which shows projections down the Cl–M–Pd–Cl unit of both structures. The P–Pd–N unit in the $RuPd(Ph_2Ppy)_2(CO)_2Cl_2$ complex is in a staggered orientation with respect to the Cartesian coordinates of the ruthenium atom and its ligands, while in $RhPd(Ph_2Ppy)_2(CO)Cl_3$ the P–Pd–N unit is halfway between an eclipsed and a staggered orientation relative to the rhodium atom and its ligands. Only two examples of bridging phosphine ligands adopting the sort of arrangement found in $RuPd(Ph_2Ppy)_2(CO)_2Cl_2$ are known. They are $Rh_2[(Et_2O_2)PNEtP(OEt)_2]_2(CO)Cl_2$ (**11**)[28] and $[Pt_2(Ph_2PCH_2PPh_2)_2(CH_3)_3]^+$ (**12**).[29]



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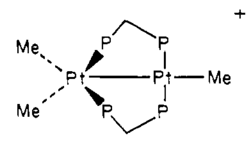

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The coordinations about the palladium atoms in $RuPd(Ph_2Ppy)_2(CO)_2Cl_2$ and $RhPd(Ppy)_2(CO)Cl_3$ are very similar as shown by their respective parameters: Pd–N, 2.126 (7), 2.13 (1) Å; Pd–Cl, 2.426 (2), 2.393 (4) Å; Pd–P, 2.190 (2), 2.220 (4) Å; P–Pd–Cl, 99.4 (1), 88.4 (1)°; N–Pd–Cl, 89.3 (1), 93.1 (3)°; N–Pd–M, 89.8 (1), 92.4 (3)°; P–Pd–M, 82.4 (1), 86.2 (1)°. The Pd–Cl distance of 2.426 (2) Å is at the long end of the range of known Pd–Cl distances (2.24–2.45 Å)[30] and probably reflects the high trans effect of the metal–metal bond.

The coordination about ruthenium is quite regular. Most of the bond angles between cis ligands lie close to the expected 90°. The greatest deviation involves the P(1)–Ru–Pd angle, which is 74.7 (1)°. The bond lengths about ruthenium fall within normal ranges and are similar to those reported for $Ru(Ph_2Ppy)(CO)_2Cl_2$.[21] The difference in the two Ru–C distances reflects the greater trans effect of the phosphine ligand, which serves to lengthen the trans Ru–C bond. The Ru–Cl distance of 2.477 (2) Å, like the Pd–Cl distance, is at the long end of the range of known Ru–Cl distances (2.51–2.39 Å).[31] This may reflect the high trans effect of the metal–metal bond.

With the structure of E ($RuPd(Ph_2Ppy)_2(CO)_2Cl_2$) known, the structure of isomer D is limited to **6** and **7**, but we still feel that there are insufficient data available to distinguish between these two possibilities. The interconversion of structures **5** and **6** could be accomplished by a twist motion and does not require bond breaking. On the other hand, isomerization between **5** and **7** requires reorientation of one Ph_2Ppy ligand. Such a reaction, the conversion of head-to-head $RhPd(Ph_2Ppy)_2(CNCH_3)_2Cl_2^+$ to the head-to-tail isomer, has been recently observed.[39] Regardless of the structure of E, it is clear that these binuclear complexes have considerable stability and remain intact through the isomerization.

Experimental Section

Preparation of Compounds. Triruthenium dodecacarbonyl was prepared according to the method described by Mantovani and Cenini.[32] $Pd_2(dba)_3{\cdot}CHCl_3$[27] and $(1,5\text{-COD})PdCl_2$[33] were prepared by established routes.

Ph_2Ppy. A solution of *n*-butyllithium (22.4 mL of a 2.4 M hexane solution, 54 mmol) was added slowly to a solution of diphenylphosphine (10 g, 54 mmol) in tetrahydrofuran (200 mL) at room temperature. The resulting red solution was stirred for $^1/_2$ h. A solution of 2-chloropyridine (5.0 g mL, 54 mmol) in tetrahydrofuran (40 mL) was then added dropwise during 1 h, at room temperature. The red color of the solution dissipated slowly upon addition of 2-chloropyridine. After this the solution was stirred overnight, 50 mL of ethanol was added, and the mixture was stirred for an additional $^1/_2$ h. Then all the solvents were removed in vacuo to give a yellow solid (13.8 g).

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(28) Haines, R. J.; Meintjies, E.; Laing, M. *Inorg. Chim. Acta* **1979**, *36*, L403–L404.

(29) Brown, M. P.; Cooper, J. J.; Frew, A. A.; Manojlovic-Muir, Lj.; Muir, K. W.; Puddephatt, R. J.; Seddon, K. R.; Thompson, M. A. *Inorg. Chem.* **1981**, *20*, 1500–1507.

(30) Steffen, W. L.; Palenik, G. J. *Inorg. Chem.* **1976**, *15*, 2432–2439.

(31) Brown, L. D.; Barnard, C. F. J.; Daniels, J. A.; Mawby, R. J.; Ibers, J. A. *Inorg. Chem.* **1978**, *17*, 2932–2935.

(32) Mantovani, A.; Cenini, S. *Inorg. Synth.* **1976**, *17*, 47–48.

(33) Chatt, J.; Vallarino, L. M.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 3413–3416.

(34) Mann, F. G.; Watson, J. *J. Org. Chem.* **1948**, *13*, 502–531.

(35) Collman, J. P.; Roper, W. R. *J. Am. Chem. Soc.* **1966**, *88*, 3504–3508.

(36) Balch, A. L.; Benner, L. S.; Olmstead, M. M. *Inorg. Chem.* 1979, *18*, 2996–3003.

(37) Calculations were performed on a Data General Eclipse computer with use of local crystallographic programs developed by H. Hope. Final refinement only was carried out with use of the SHELXTL (July 1981) program package.

(38) Definitions are as follows: $R = \sum||F_o| - |F_c||/\sum|F_o|$; the quantity minimized during final refinement was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F_o) + 0.001F_o^2$. In the initial stages of solution a Hughes weighting scheme was employed.

(39) Farr, J. P.; Balch, A. L., unpublished observations.

The product was extracted by dissolution in hot hexane (800 mL) to give a light yellow solution. After treatment by charcoal, filtration of the resulting colorless solution, and evaporation of the solvent, the pure product was obtained as white crystals having a melting point of 82 °C (lit.[34] mp 84–85 °C) (13.25 g, 94% yield based on PPh_2H). The identity of the product was confirmed by comparison of the infrared spectrum and the ${}^{31}P\{{}^1H\}$ NMR spectrum with those of an authentic sample.

$[Ru(CO)_3(Ph_2Ppy)]_3$. This was prepared according to the method described for the triphenylphosphine analogue.[17] Triruthenium dodecacarbonyl (0.46 g, 0.72 mmol) was dissolved in methanol (20 mL) and a threefold excess of 2-(diphenylphosphino)pyridine (0.64 g, 2.4 mmol) added. Upon reflux for 5 h, a dark violet precipitate was formed. This precipitate was collected, washed with methanol, and dried in vacuo (0.70 g, 73% yield). It may be recrystallized from dichloromethane/diethyl ether. Anal. Calcd for $C_{60}H_{42}N_3O_9P_3Ru_3$: C, 53.57; H, 3.15; N, 3.12. Found: C, 53.55; H, 3.21; N, 3.11.

$(Ph_2Ppy)_2Ru(CO)_3$. This was prepared by an adaptation of reported procedures for the PPh_3 analogue.[18,19] Triruthenium dodecacarbonyl (0.40 g, 0.63 mmol) was dissolved in dioxygen-free hexane (400 mL), and an excess of Ph_2Ppy (0.99 g, 3.8 mmol) was added under an inert atmosphere. After irradiation of the orange solution at 25 °C with a UV lamp at $\lambda > 390$ nm (2 M $NaNO_2$ filter) for 5 h, a pale yellow precipitate had formed. This precipitate was collected, washed with hexane, and dried in vacuo (1.02 g, 76% yield). It was recrystallized from dichloromethane/ethyl ether to give pale yellow crystals. Anal. Calcd for $C_{37}H_{28}N_2O_3P_2Ru$: C, 62.48; H, 3.97; N, 3.94. Found: C, 62.47; H, 3.92; N, 3.90.

$Ru(Ph_2Ppy)_2(CO)_2Cl_2$. This follows the work of Collman and Roper.[20] A stream of dichlorine was bubble for a few seconds through a yellow solution of $Ru(CO)_3(PPh_2py)_2$ (0.71 g) in dichloromethane (35 mL) at room temperature. The infrared spectrum (ν_{CO} 2143 w, 2085 vs, 2052 s cm^{-1}) of the resulting pale yellow solution indicated the complete transformation of the starting material into the ionic species $[Ru(CO)_3Cl(PPh_2Py)_2]^+Cl^-$ (identified by analogy with the infrared spectrum of $[Os(CO)_3Br(Ph_3P)_2]^+Br^-$ in the CO stretching region[35]). Upon reflux for 6 h, decarbonylation of the cation occurred to give the title compound quantitatively as indicated by the evolution of its infrared spectrum. The solvent was then evaporated, and the solid residue was crystallized from dichloromethane/ethyl ether. White crystals (0.57 g, 76% yield) of $Ru(Ph_2Ppy)_2(CO)_2Cl_2$ were obtained. The compound crystallizes in the space group *Pbca* (No. 61) with $a = 16.44$ (1), $b = 21.05$ (1), and $c = 19.60$ (1) Å. Anal. Calcd for $C_{36}H_{28}N_2B_2Cl_2P_2Ru$: C, 57.30; H, 3.75; N, 3.71; Cl, 9.40. Found: C, 57.06; H, 3.82; N, 3.63; Cl, 9.71.

Reaction of $Ru(Ph_2Ppy)_2(CO)_3$ with (1,5-COD)$PdCl_2$. Treatment of a colorless solution of $Ru(Ph_2Ppy)_2(CO)_3$ (0.498 g, 0.70 mmol) in dichloromethane (25 mL) with an excess of yellow (1,5-COD)$PdCl_2$ (0.244 g, 0.86 mmol) in dichloromethane (20 mL) produced, within a few seconds, a deep red-brown solution. The infrared spectrum of this solution exhibited carbon monoxide stretching absorptions at 2065 vs, 2005 vs, br, and 1955 m cm^{-1} while the ${}^{31}P\{{}^1H\}$ NMR spectrum showed resonances due to five compounds: A, 4.44 ppm, singlet, 38% yield; B, −6.84 ppm, singlet, 31%; C, 21.49 ppm, singlet, 16%; D, 38.88 ppm, doublet, 17.95 ppm, doublet, $J(P,P) = 7.5$ Hz, 8%; E, 20.14 ppm, doublet; 16.54 ppm, doublet, $J(P,P) = 2$ Hz, 7%. The solution was filtered and the solvent was removed in vacuo to give a red-brown solid (0.56 g). Fractional crystallization of the crude product from dichloromethane by the gradual addition of ethyl ether gave successively a crop of red crystals and a crop of white crystals. The red crystals, which showed no infrared absorption in the carbonyl region (2200–1600 cm^{-1}), were identified as A by the presence of a ${}^{31}P$ NMR resonance at 4.4 ppm. The white crystals had infrared absorptions at 2067 vs and 2007 vs cm^{-1} in dichloromethane solution and were identified as B by a ${}^{31}P$ NMR resonance at −6.84 ppm. The solution that remained after the removal of these two species was evaporated to dryness, and the orange residue was dissolved in a minimum volume of methanol to give an orange solution and a white solid. This white solid was identified as C by ${}^{31}P$ NMR spectroscopy (singlet at 21.5 ppm) and had carbonyl absorptions at 2062 s and 2002 vs cm^{-1} in dichloromethane solution. The remaining methanolic solution was cooled and stored at −5 °C. Yellow needles (ν_{CO} 2013 vs, 1954 vs cm^{-1}; ${}^{31}P$ NMR 38.8 ppm (doublet, $J = 7.5$ Hz), 17.9 ppm (doublet, $J = 7.5$ Hz)) were deposited and identified as compound D. Further concentration and cooling of the remaining solution gave orange crystals of compound E (ν_{CO} 2025 vs, 1965 vs; ${}^{31}P$ NMR 20.1 ppm (doublet, $J = 2$ Hz), 16.5 ppm (doublet, $J = 2$ Hz)).

$Pd(Ph_2Ppy)_2Cl_2\cdot 1.7CH_2Cl_2$. A solution containing 0.505 g (1.3 mmol) of $Pd(C_7H_5N)_2Cl_2$ in 10 mL of dichloromethane was added dropwise to a solution containing 0.74 g (2.8 mmol) of Ph_2Ppy also in dichloromethane. Yellow crystals were precipitated by the dropwise addition of ethyl ether. The crystals were collected by filtration, washed with ethyl ether, and vacuum dried; yield 0.916 g, 99%. The presence of dichloromethane was confirmed by ${}^1H$ NMR in $CDCl_3$. Integration of the CH_2Cl_2 peak vs. the phenyl region gave a ratio of 3.4:28. Anal. Calcd for $C_{34}H_{28}Cl_2N_2P_2Pd\cdot 1.7CH_2Cl_2$: C, 50.5; H, 3.73; N, 3.30; Cl, 22.57. Found: C, 50.45; H, 3.87; N, 3.19; Cl, 22.71.

$Pd_2(Ph_2Ppy)_2Cl_2$. A deep violet solution of $Pd_2(dba)_3\cdot CHCl_3$ (0.094 g, 0.09 mmol) in dichloromethane (20 mL) was added to a stirred suspension of $Pd(Ph_2Ppy)_2Cl_2$ (0.128 g, 0.18 mmol) in dichloromethane (25 mL). After being stirred for 1 h, the dark red solution was filtered. The solution was concentrated under vacuum to ca. 5 mL, and ethyl ether was added dropwise to the solution. The dark red crystals of the product that deposited were collected by filtration, washed with ethyl ether, and dried under vacuum (yield 90%). Anal. Calcd for $C_{34}H_{28}N_2Cl_2P_2Pd_2$: C, 50.39; H, 3.49; N, 3.46. Found: C, 49.23; H, 3.54; N, 3.30.

$RuPd(Ph_2Ppy)_2(CO)_2Cl_2$. A solution of $Ru(Ph_2Ppy)_2(CO)_2Cl_2$ (0.413 g, 0.55 mmol) and $Pd_2(dba)_3\cdot CHCl_3$ (0.284 g, 0.27 mmol) in dichloromethane (60 mL) was heated under reflux for 2 h. The solution was filtered, and the filtrate was evaporated to dryness under vacuum. The solid was redissolved in a minimum volume of dichloromethane and transferred onto a wet-packed 27 × 2 cm silica gel chromatography column. Elution of the column with a 5:1 v/v mixture of dichloromethane/acetone produced five bands with the following characteristics: first band, yellow, contains $Ru(Ph_2Ppy)(CO)_2Cl_2$ and $RuPd(Ph_2Ppy)_2(CO)_2Cl_2$; second band red, contains $RuPd(Ph_2Ppy)_2(CO)_2Cl_2$, isomer E; third band, yellow, contains $RuPd(Ph_2Ppy)_2(CO)_2Cl_2$, isomers D and E; fourth band, orange, contains $RuPd(Ph_2Ppy)_2(CO)_2Cl_2$, isomer D; fifth band, yellow contains $RuPd(Ph_2Ppy)_2(CO)_2Cl_2$, isomer D. Band composition was determined by infrared and ${}^{31}P$ NMR spectroscopy. Bands 4 and 5 were combined, and their volume was reduced to 5 mL. The dropwise addition ethyl ether produced 0.11 g (23%) of ochre crystals of $RuPd(Ph_2Ppy)_2(CO)_2Cl_2\cdot 0.5CH_2Cl_2$, isomer D. Anal. Calcd for $C_{36.5}H_{29}N_2O_2Cl_3P_2RuPd$: C, 48.52; H, 3.24; N, 3.10; Cl, 11.77. Found: C, 47.92; H, 3.42; N, 3.05; Cl, 11.45. Band 2 was evaporated to 3 mL. The dropwise addition of ethyl ether produced orange crystals of isomer E, which were collected by filtration, washed with ether, and vacuum dried (yield 0.2 g, 4.2%). The composition of isomer E was confirmed by the X-ray crystallographic study reported in the next section.

$RuPd(Ph_2Ppy)_2(CO)_2Cl_2\cdot 1.25CH_2Cl_2$. X-ray Data Collection. A dark yellow crystal of isomer E of dimensions 0.12 × 0.20 × 0.20 mm was found to be suitable for X-ray data collection. The crystal was mounted on the goniometer head of a Syntex $P2_1$ diffractometer in a cold stream of $N_2(g)$, which maintained the crystal temperature at 140 K. The radiation used was graphite-monochromated Mo Kα (λ 0.710 69 Å). A typical reflection, located by using a rotation photograph, had a width at half-height of 0.4° on an ω scan. With use of procedures described elsewhere[21] the space group was found to be $P2_1/c$ (No. 14) and the density 1.61 g cm^{-3}, indicating $Z = 4$ (fw 967.14). A least-squares fit of 16 reflections with $30° < 2\theta < 43°$ yielded cell dimensions $a = 10.493$ (2) Å, $b = 17.685$ (4) Å, $c = 21.470$ (5) Å, $\beta = 92.07$ (2)°, and $V = 3982$ (1) Å^3.

Data were collected with use of an ω scan of 1° range and speed ranging from 2 to 60°/min. Stationary-background counts were collected with a 1° offset from the center of the peak. Two check reflections were monitored throughout and showed only a random fluctuation. Reflections were collected to $2\theta = 45°$, yielding 5387 unique data. The data were corrected for Lorentz and polarization effects but not for absorption (μ(Mo Kα) = 12.3 cm^{-1}). For a crystal of the dimensions given the absorption correction factors range from 1.28 to 1.51. Reduction of the data to F_o and $\sigma(F_o)$ were as previously described.[36]

Solution and Refinement of the Structure. The structure was solved by finding two metal atoms on a Patterson map.[37] Four chlorine atoms (two of these were from a molecule of crystallization of CH_2Cl_2), two phosphorus atoms, and one nitrogen atom were located on a first Fourier map. Full-matrix least-squares refinement of these atoms brought R to 0.26.[38] The remaining atoms were located on a second Fourier map except for a partially occupied second CH_2Cl_2 molecule, which was assigned an estimated occupancy of 0.25 on the basis of its intensity in a difference Fourier map. Full-matrix least-squares refinement of all non-hydrogen atoms using isotropic thermal parameters yielded an *R* of 0.060. The final stage of refinement made use of the blocked-cascade least-squares method and a riding model for hydrogen atoms in which a hydrogen atom was given a computed position and assigned a thermal parameter 1.2 times that of the carbon atom to which it was bonded. In addition, the atoms Ru, Pd, Cl(1), Cl(2), P(1), P(2), C(1), C(2), O(1), and O(2) of the title compound, as well as the fully occupied molecule of dichloromethane, were given anisotropic thermal parameters. This brought the number of parameters to 274, yielding *R* of 0.043, $R_w = 0.049$, by using 4605 reflections ($I > 3\sigma(I)$). Neutral-atom scattering factors and corrections for anomalous dispersion for Pd, Ru, Cl, and P were from ref 40. Positional and isotropic thermal parameters, hydrogen atom coordinates, anisotropic thermal parameters, and structure factor tables are available as supplementary material.

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Registry No. A, 78055-58-0; B, 78790-90-6; C, 78790-91-7; D, 82648-72-4; E, 82690-70-8; [Ru(CO)$_3$(Ph$_2$Ppy)]$_3$, 82690-69-5; (Ph$_2$Ppy)$_2$Ru(CO)$_3$, 82648-71-3; Pd(Ph$_2$Ppy)$_2$Cl$_2$, 78088-45-6; Ru$_3$(CO)$_{12}$, 15243-33-1; (1,5-COD)PdCl$_2$, 12107-56-1; Pd(PhCN)$_2$Cl$_2$, 14220-64-5; Pd$_2$(dba)$_3$, 51364-51-3; Ru, 7440-18-8; Pd, 7440-05-3.

Supplementary Material Available: Anisotropic temperature factors (Table V), hydrogen coordinates (Table VI), a stereoscopic view of RuPd(Ph$_2$Ppy)$_2$ (CO)$_2$Cl$_2$, isomer E (Figure 4), and a table of structure factors for RuPd(Ph$_2$Ppy)$_2$(CO)$_2$Cl$_2$ (31 pages). Ordering information is given on any current masthead page.

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(40) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Contribution from the Department of Chemistry,
The University of North Carolina, Chapel Hill, North Carolina 27514

Concerning the Absorption Spectra of the Ions M(bpy)$_3^{2+}$ (M = Fe, Ru, Os; bpy = 2,2′-Bipyridine)

EDWARD M. KOBER* and THOMAS J. MEYER

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An electronic structural model, which includes spin–orbit coupling, is developed for the absorption spectra of the ions M(bpy)$_3^{2+}$ (M = Fe, Ru, Os; bpy = 2,2′-bipyridine). It is found that, even for Os, the excited states can be classified as "singlets" and "triplets" although there is considerable mixing between the pure spin states. Consequently, the luminescent excited states of Ru(bpy)$_3^{2+}$ and Os(bpy)$_3^{2+}$ are assigned as being states largely "triplet" in character. Explicit assignments of the absorption spectra for the complexes are proposed. The implications of the present treatment relative to other theoretical analyses are discussed.

Introduction

Polypyridyl complexes of the type Ru(bpy)$_3^{2+}$ and Os(bpy)$_3^{2+}$ (bpy = 2,2′-bipyridine) have been studied intensively[1] in part because of possible applications of their metal to ligand charge transfer (MLCT) excited states in energy conversion processes.[2] Despite their importance, the electronic structures of the MLCT excited states have not been clearly delineated. In particular, three rather fundamental questions have not been totally resolved: (1) Is the promoted electron localized in the π^* levels of a single bpy ligand or is it delocalized over the π^* orbitals of all three bpy ligands?[3–5] (2) Can the lower lying excited states be characterized as being triplet states or is such a description meaningless?[5,6] (3) Why is the excited-state lifetime of Os(bpy)$_3^{2+}$ so much shorter than that of Ru(bpy)$_3^{2+}$?[5,7,8]

Pertinent information concerning each of the three questions is obtainable from an analysis of electronic absorption spectra. Recently, the polarized absorption spectra (at 8 K) of the M(bpy)$_3^{2+}$ ions (M = Fe, Ru, Os) doped into single crystals of Zn(bpy)$_3^{2+}$ salts have been reported.[6] It was noted that the intensity of the lowest lying MLCT transitions relative to the strongest MLCT transitions increased dramatically in the series Fe < Ru < Os. The increase was found to be proportional to λ^2, where λ is the spin–orbit coupling constant of the metal, and it was inferred that lowest energy bands were transitions to "triplet" states into which appreciable singlet character was mixed via spin–orbit coupling. It was also found that the absorption spectrum of Os(bpy)$_3^{2+}$ was much more complex than that of the other ions, and it has been suggested that spin–orbit coupling could be responsible for the increased complexity as well.[6,9] Neither of these latter two points was

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* To whom correspondence should be addressed at Department of Chemistry, Indiana University, Bloomington, IN 47405.

(1) See, for example: (a) Chan, M.-S.; Wahl, A. C. *J. Phys. Chem.* **1978**, *82*, 2542–9. (b) Van Houten, J.; Watts, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 4853–8. (c) McCaffery, A. J.; Mason, S. F.; Norman, B. J. *J. Chem. Soc. A* **1969**, 1428–41. (d) Rillema, D. P.; Jones, D. S.; Levy, H. A. *J. Chem. Soc., Chem. Commun.* **1979**, 849–51. (e) References therein.

(2) (a) Meyer, T. J. *Acc. Chem. Res.* **1978**, *11*, 94–100. (b) Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1–64. (c) Whitten, D. G. *Acc. Chem. Res.* **1980**, *13*, 83–90. (d) Sutin, N.; Creutz, C. *Adv. Chem. Ser.* **1978**, *No. 168*, 1–27. (e) Humphry-Baker, R.; Lilie, J.; Grätzel, M. *J. Am. Chem. Soc.* **1982**, *104*, 422–5.

(3) (a) Bradley, P. G.; Kress, N.; Hornberger, B. A.; Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 7441–6. (b) Dallinger, R. F.; Woodruff, W. H. *Ibid.* **1979**, *101*, 4391–3.

(4) Hipps, K. W. *Inorg. Chem.* **1980**, *19*, 1390–2.

(5) (a) Hager, G. D.; Crosby, G. A. *J. Am. Chem. Soc.* **1975**, *97*, 7031–7. (b) Hipps, K. W.; Crosby, G. A. *Ibid.* **1975**, *97*, 7042–8. (c) Harrigan, R. W.; Crosby, G. A. *J. Chem. Phys.* **1973**, *59*, 3468–76.

(6) (a) Felix, F.; Ferguson, J.; Güdel, H. U.; Ludi, A. *Chem. Phys. Lett.* **1979**, *62*, 153–7. (b) Felix, F.; Ferguson, J.; Güdel, H. U.; Ludi, A. *J. Am. Chem. Soc.* **1980**, *102*, 4096–102. (c) Decurtins, S.; Felix, F.; Ferguson, J.; Güdel, H. U.; Ludi, A. *Ibid.* **1980**, *102*, 4102–6.

(7) (a) Lacky, D. E.; Pankuch, B. J.; Crosby, G. A. *J. Phys. Chem.* **1980**, *84*, 2068–74. (b) Demas, J. N.; Crosby, G. A. *J. Am. Chem. Soc.* **1971**, *93*, 2841–7.

(8) (a) Allsopp, S. R.; Cox, A.; Kemp, T. J.; Reed, W. J.; Carassiti, V.; Traverso, O. *J. Chem. Soc., Faraday Trans. 1* **1979**, *74*, 353–62. (b) Allsopp, S. R.; Cox, A.; Kemp, T. J.; Reed, W. J. *Ibid.* **1978**, *73*, 1275–89.

(9) Ceulemans, A.; Vanquickenborne, L. G. *J. Am. Chem. Soc.* **1981**, *103*, 2238–41.

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