

Synthesis of Asymmetric Rh₂⁴⁺ Complexes. X-ray Crystal Structure of Rh₂(form)₃(NO₃)(PPh₃)·0.5CH₂Cl₂ and Rh₂(form)₃(NO₃)(C₅H₅N) (form = N,N'-Di-*p*-tolylformamidinate)

Pasquale Piraino,* Giuseppe Bruno, Giuseppe Tresoldi, Sandra Lo Schiavo, and Francesco Nicolò

Received February 22, 1988

The reaction of the paramagnetic Rh₂⁵⁺ complex Rh₂(form)₃(NO₃)₂ (form = N,N'-di-*p*-tolylformamidinate) with an excess of the neutral ligands PPh₃, pyridine, and dimethylamine leads, via reductive elimination of one nitrate group, to the formation of the asymmetric Rh₂⁴⁺ complexes Rh₂(form)₃(NO₃)L (L = PPh₃ (1), pyridine (2), N(CH₃)₂H (3)). The two rhodium atoms in complexes 1–3 display different coordinations and reduced average formal oxidation states. The complexes have been characterized by IR, ³¹P NMR, and ¹⁰³Rh NMR spectroscopic methods, which point out the nonequivalence of the two rhodium atoms. Complexes 1 and 2 have been also characterized by single-crystal X-ray analysis. Complex 1 belongs to the monoclinic space group system P2₁/n, with *a* = 21.529 (3) Å, *b* = 23.990 (3) Å, *c* = 11.944 (1) Å, β = 102.13 (4)°, *Z* = 4, and *R* = 0.057 for 2046 reflections with *I* > 3σ(*I*). The crystal structure reveals that one of the three formamidinate groups spanning the dimetal center (Rh–Rh = 2.498 (2) Å) is bonded in an unusual way, namely, σ,σ-N,N' with a localized double bond. Complex 2 forms monoclinic crystals in space group P2₁/c with *a* = 10.238 (1) Å, *b* = 16.567 (2) Å, *c* = 28.356 (4) Å, β = 95.56 (3)°, *Z* = 4, and *R* = 0.041 for 3392 reflections with *I* > 3σ(*I*). In complexes 2 and 3 all of the bridging ligands are bonded in the usual fashion, namely σ,σ-N,N' with delocalized double bonds.

Introduction

Recently we have found that the formamidinate anion, which may exhibit a number of metal coordination geometries,¹ acts as strong binucleating ligand leading to the stabilization of the Rh₂⁴⁺ and Rh₂⁵⁺ cores.² In all the complexes that we isolated as well as in complexes containing similar systems,³ the N-C-N fragment is σ,σ-N,N'-bonded to the dimetal center with a delocalized π-electron system. Furthermore, while it is well documented that the symmetric arrangement of the bridging ligands around the Rh₂⁴⁺ core leads to complexes with nonpolar Rh–Rh bonds,⁴ few examples of asymmetric Rh₂⁴⁺ complexes have been reported.⁵

We wish to report our results concerning the reduction of the Rh₂⁵⁺ complex Rh₂(form)₃(NO₃)₂ (form = N,N'-di-*p*-tolylformamidinate anion) by neutral ligands such as PPh₃, pyridine, and N(CH₃)₂H leading to the unprecedented, asymmetric Rh₂⁴⁺ complexes Rh₂(form)₃(NO₃)L [L = PPh₃ (1), C₅H₅N (2), N(CH₃)₂H (3)]. In these complexes the two rhodium atoms display different coordinations and reduced average formal oxidation states. We also report the X-ray analysis of complexes 1 and 2, which shows the peculiar bonding situation in the triphenylphosphine derivative. This exhibits, in fact, one of the formamidinate groups bridging the dirhodium unit in an unusual fashion, namely σ,σ-N,N' with a localized double bond.

Experimental Section

Rh₂(form)₃(NO₃)₂ was prepared by the literature procedure.^{2a} Infrared spectra were recorded with a Perkin-Elmer 783 instrument. ³¹P and ¹⁰³Rh NMR spectra were recorded on Bruker SY-80 and WH-400 spectrometers, respectively. The reactions were carried out either under a purified N₂ atmosphere or in air.

Preparation of Rh₂(form)₃(NO₃)PPh₃ (1). Triphenylphosphine (0.314 g, 1.2 mmol) was added to a stirred solution of Rh₂(form)₃(NO₃)₂ (0.4 g, 0.4 mmol) in acetone (20 mL). The reaction mixture was stirred at room temperature for 24 h during which time the blue solution turned

red-orange. The solvent was evaporated and the residue repeatedly washed with 5-mL portions of petroleum ether (bp 40–60 °C). Crystallization was carried out from a benzene–heptane mixture, affording 0.33 g of complex (yield 66%). By evaporation of the petroleum ether extract, 200 mg of Ph₃PO was also obtained. Anal. Calcd for C₆₃H₆₀N₇O₃PRh₂: C, 63.05; H, 5.04; N, 8.17; P, 2.58. Found: C, 62.82; H, 4.95; N, 8.40; P, 2.7. Infrared spectrum (KBr pellet; cm⁻¹): ν(N=C=N) 1585 (vs) and 1620 (s). ³¹P NMR (30 °C, CDCl₃): δ 29.4 (dd, ¹J_{P-Rh} = 145 Hz, ²J_{P-Rh} = 5.78 Hz). ¹⁰³Rh NMR (30 °C, CDCl₃): δ 6472 (d, J_{Rh-Rh} = 34 Hz), 3007 (dd, J_{Rh-P} = 145 Hz).

Preparation of Rh₂(form)₃(NO₃)(C₅H₅N) (2). To a solution of Rh₂(form)₃(NO₃)₂ (0.25 g, 0.25 mmol) in benzene (20 mL) was added pyridine (0.15 mL). After the mixture was stirred at 60 °C for 40 h, the resultant green-yellow solution was concentrated under vacuum. To the oil residue was added 20 mL of petroleum ether (bp 40–60 °C), and the mixture was stirred for 10 min. After filtration the greenish residue was crystallized from diethyl ether–heptane; yield 43%. Anal. Calcd for C₅₀H₅₀N₈O₃Rh₂: C, 59.06; H, 4.95; N, 11.01; O, 4.71. Found: C, 59.18; H, 5.0; N, 11.24; O, 4.90. Infrared spectrum (KBr pellet; cm⁻¹): ν(N=C=N) 1580 (vs). ¹⁰³Rh NMR (30 °C, CDCl₃): δ 6060 (d), 4332 (d, J_{Rh-Rh} = 40 Hz).

Preparation of Rh₂(form)₃(NO₃)N(CH₃)₂H (3). To a solution of Rh₂(form)₃(NO₃)₂ (0.2 g, 0.2 mmol) in 20 mL of benzene was added N(CH₃)₂H (0.5 mL). The original blue solution rapidly lightened and became yellow-brown. After 3-h reaction time the volatiles were removed in vacuo and the solid residue was extracted with several portions of *n*-heptane. Reducing and cooling the extracts gave 0.1 g of 3. An additional crop of green crystals was collected from the mother liquor. The combined yields were 60%. Anal. Calcd for C₄₇H₅₂N₈O₃Rh₂: C, 57.44; H, 5.33; N, 11.40; O, 4.88. Found: C, 57.52; H, 5.41; N, 11.45; O, 4.96. Infrared spectrum (KBr pellet; cm⁻¹): ν(N=C=N) 1585 (vs).

X-ray Data Collection and Structure Refinement. Suitable red-orange crystals of 1 and greenish crystals of 2 were grown by slow evaporation of the solvent from a dichloromethane–hexane and benzene–heptane solutions, respectively. Diffraction data were collected on a Siemens-Stoe four-circle diffractometer by using graphite-monochromated Mo Kα (λ = 0.71069 Å) radiation. Accurate unit cell dimensions and crystal orientation matrices for complexes 1 and 2 were obtained from least-squares refinement of 2θ, ω, χ, and φ values of 20 strong reflections in the range 15° < 2θ < 26°. Lorentz and polarization corrections were applied to the intensity data, but no absorption correction was made due to the low absorption coefficient (μ = 6.1 and 6.5 cm⁻¹ for 1 and 2, respectively) and the fairly uniform dimensions of the crystals. Extinction corrections were ignored. During the course of the intensity data collection, the crystals showed no loss in intensity. Crystallographic data and other pertinent information are summarized in Table I. The structures of 1 and 2 were solved by using standard Patterson methods, successive least-squares refinements, and difference Fourier maps.

Anisotropic temperature factors were introduced for all non-hydrogen atoms except those belonging to the phenyl and tolyl rings. These were refined isotropically for compound 1 and as rigid groups for compound 2 and restricted to their normal geometry (*D*_{6h} symmetry; *d*(C–C) = 1.395 Å) by using the group refinement procedure. Each ring was as-

- (1) Grove, D. M.; Van Koten, G.; Ubbels, H. J. C.; Vrieze, K.; Niemann, L. C.; Stam, C. H. *J. Chem. Soc., Dalton Trans.* 1986, 717.
- (2) (a) Piraino, P.; Bruno, G.; Nicolò, F.; Faraone, F.; Lo Schiavo, S. *Inorg. Chem.* 1985, 24, 4760. (b) Piraino, P.; Bruno, G.; Tresoldi, G.; Lo Schiavo, S.; Zanello, P. *Ibid.* 1987, 26, 91. (c) Piraino, P.; Bruno, G.; Lo Schiavo, S.; Laschi, F.; Zanello, P. *Ibid.* 1987, 26, 2205.
- (3) Cotton, F. A.; Isley, W. H.; Kaim, W. *Inorg. Chem.* 1980, 19, 2360 and references therein.
- (4) (a) Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*; Wiley-Interscience: New York, 1982. (b) Felthouse, T. R. *Prog. Inorg. Chem.* 1982, 29, 73. (c) Boyer, E. B.; Robinson, S. D. *Coord. Chem. Rev.* 1983, 50, 109.
- (5) (a) Lifsey, R. S.; Chavan, M. Y.; Chau, L. K.; Ahsan, M. Q.; Kadish, K. M.; Bear, J. L. *Inorg. Chem.* 1987, 26, 82 and references therein. (b) Cotton, F. A.; Barcelo, F.; Lahuerta, P.; Llusar, R.; Ubeda, M. A. *Inorg. Chem.* 1988, 27, 1010.

Table I. Crystal and Refinement Data for $\text{Rh}_2(\text{form})_3(\text{NO}_3)(\text{PPh}_3)\cdot 0.5\text{CH}_2\text{Cl}_2$ (**1**) and $\text{Rh}_2(\text{form})_3(\text{NO}_3)(\text{C}_5\text{H}_5\text{N})$ (**2**)

	1	2
formula	$\text{C}_{63}\text{H}_{60}\text{Rh}_2\text{PN}_7\text{O}_3\cdot 0.5\text{CH}_2\text{Cl}_2$	$\text{C}_{50}\text{H}_{50}\text{N}_8\text{O}_3\text{Rh}_2$
fw	1242.45	1016.67
space group	$P2_1/n$	$P2_1/c$
<i>a</i> , Å	21.529 (3)	10.238 (1)
<i>b</i> , Å	23.990 (3)	16.567 (2)
<i>c</i> , Å	11.944 (1)	28.356 (4)
β , deg	102.13 (4)	95.56 (3)
<i>V</i> , Å ³	6031.5 (5)	4787.0 (8)
<i>Z</i>	4	4
d_{calcd} , g/cm ³	1.37	1.34
cryst size, mm	0.10 × 0.13 × 0.08	0.08 × 0.10 × 0.12
cryst habit	prismatic	prismatic
orientatn reflcn: no.:	20; 15 < 2θ < 26	20; 15 < 2θ < 26
range (2θ), deg		
<i>T</i> , °C	21	21
abs coeff, cm ⁻¹	6.1	6.5
radiation	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)
monochromator	graphite cryst	graphite cryst
scan type	2θ-ω	2θ-ω
scan speed, deg s ⁻¹	0.03	0.03
scan range, deg	1.2	1.2
reflcn measd	± <i>h</i> , + <i>k</i> , + <i>l</i>	± <i>h</i> , + <i>k</i> , + <i>l</i>
data limits	3 < 2θ < 50	3 < 2θ < 50
tot. no. of reflcn data	5630	8036
<i>R</i> _{int}	0.028	0.025
no. of colld obsd data	2046 [<i>I</i> > 3σ(<i>I</i>)]	3392 [<i>I</i> > 3σ(<i>I</i>)]
no. of params refined	288	283
max Δ/σ for the last cycle	0.04	0.005
<i>R</i> ^a	0.057	0.041
<i>R</i> ^b	0.053	0.040

$$^a R = [\sum |F_o| - |F_c| / \sum |F_o|]. \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}.$$

signed an individual isotropic thermal parameters. Hydrogen atoms in both the compounds were added at calculated positions and included in the structure factor calculations with a common thermal parameter ($U = 0.06 \text{ \AA}^2$). The weighting scheme used in the last refinement cycles was: $w = 1.8209/(\sigma^2|F_o| + 0.000305|F_o|^2)$ for **1** and $w = 1.3545/(\sigma^2|F_o| + 0.000188|F_o|^2)$ for **2**, which showed reasonable consistency in a test of $w\Delta^2$ for data sectioned with respect to both $|F_o|$ and $(\sin \theta)/\lambda$. Scattering factors for non-hydrogen atoms were taken from ref 6 and for hydrogen atoms from ref 7. Anomalous dispersion corrections for Rh and P atoms were taken from ref 8.

All calculations were performed with the SHELX 76⁹ and PARST¹⁰ sets of programs on the IBM 4341 computer at the "Centro di Calcolo dell'Università di Messina". The refined structures were plotted with use of the ORTEP program. Distances and angles associated with the tolyl and phenyl fragments, and the nitrate groups (Tables SI and SII), hydrogen atom parameters (Tables SIII and SIV), temperature factors (Tables SV and SVI), and structure factors are available as supplementary material.

Results and Discussion

Treatment over a period of 24 h of an acetone solution of the paramagnetic Rh_2^{5+} complex $\text{Rh}_2(\text{form})_3(\text{NO}_3)_2$ ^{2a} with an excess of triphenylphosphine (molar ratio 1:3) gives the diamagnetic complex **1**. Triphenylphosphine oxide was also recovered as by-product. Structural assignment is based upon the spectral data and the single-crystal X-ray analysis. The ³¹P NMR spectrum of complex **1**, consistent with the structure of Figure 2, exhibits the X part of an AMX pattern as a doublet of doublets centered at δ 29.4 with one large (145 Hz) and one small (5.78 Hz) coupling to Rh(1) and Rh(2), respectively. The relatively small ²*J*_{P-Rh} is consistent with the equatorial position of the phosphine. The magnetic inequivalence of the rhodium atoms is proved by the

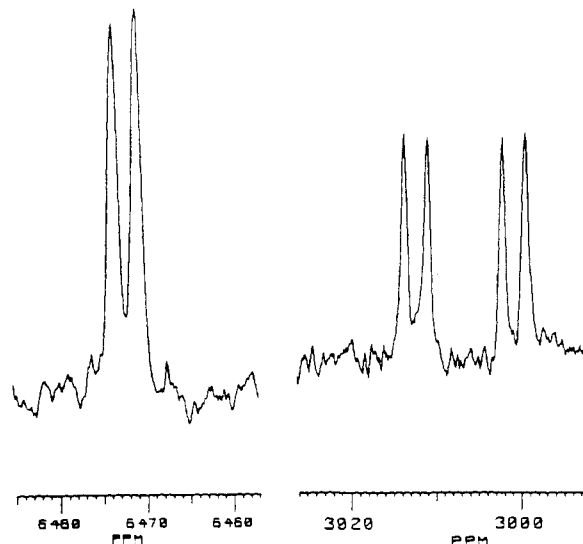


Figure 1. ¹⁰³Rh NMR spectrum (30 °C, CDCl_3) of $\text{Rh}_2(\text{form})_3(\text{NO}_3)(\text{PPh}_3)$ (**1**).

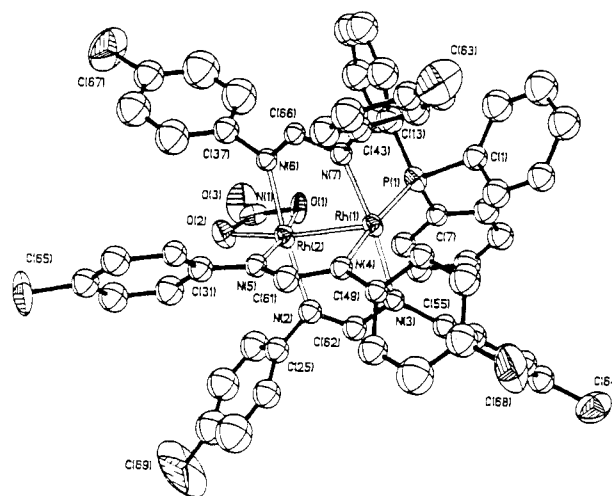
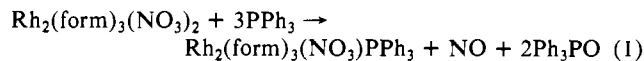


Figure 2. Molecular structure and atom-labeling scheme for $\text{Rh}_2(\text{form})_3(\text{NO}_3)(\text{PPh}_3)$ (**1**).

¹⁰³Rh NMR spectrum (Figure 1), which shows two resonances at δ 6472 (d, $J_{\text{Rh-Rh}} = 34 \text{ Hz}$) and 3007 (dd). Although few ¹⁰³Rh NMR data have been reported for Rh_2^{4+} complexes,^{11,12} the above resonances lie in the range (3000–8000 ppm) until now quoted for this class of compounds. The $J_{\text{Rh-Rh}}$ value of 34 Hz is in good agreement with the value found for the asymmetric complex $[\text{Rh}_2(\text{mhp})_4]_2$ (mhp = 6-methyl-2-hydroxypyridinato) (34 Hz)¹¹ but it is very different from the values of 7.9 and 8 Hz reported for the complexes $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4[\text{P}(\text{OMe})_3]_2$ ^{12a} and $\text{Rh}_2(\text{O}_2\text{C-CF}_3)_4\text{L}_2$ (L = PPh_3 , PCy_3)^{12b} not containing polar Rh–Rh bonds. In the IR spectrum the complex shows two strong absorptions at 1585 and 1620 cm^{-1} resulting, very likely, from two different N–C–N fragments.

The process by which complex **1** is formed is clearly complex; we suggest the reaction occurs via reductive elimination of one nitrate group by PPh_3 according to eq 1. The net reaction can



be considered as reduction of one metal center by PPh_3 , which then serves as ligand to the reduced metal center. The proposed equation for the formation of **1** is supported by the ratio starting complex: PPh_3 (1:3) necessary to effect the reaction and by the

- (6) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffraction, Gen. Theor. Crystallogr.* **1968**, *24*, 321.
 (7) Stewart, R. F. *J. Chem. Phys.* **1970**, *53*, 3175.
 (8) Cromer, D. T.; Libermann, D. *J. Chem. Phys.* **1970**, *53*, 1981.
 (9) Sheldrick, G. M. "SHELX 76 Computing System"; University of Cambridge: Cambridge, England, 1976.
 (10) Nardelli, M. *Comput. Chem.* **1983**, *7*, 95.

- (11) Garner, C. D.; Berry, M.; Mann, B. E. *Inorg. Chem.* **1984**, *23*, 1501.
 (12) (a) Boyar, E. B.; Robinson, S. D. *Inorg. Chim. Acta* **1982**, *64*, L193.
 (b) Teiser, J.; Drago, R. S. *Inorg. Chem.* **1986**, *25*, 2989.

Table II. Selected Bond Distances (Å) and Angles (deg) for Rh₂(form)₃(NO₃)(PPh₃) (1)

Bond Distances			
Rh(1)-Rh(2)	2.498 (2)		
Rh(1)-N(3)	2.074 (15)	N(1)-O(1)	1.285 (21)
Rh(1)-N(4)	2.025 (16)	N(1)-O(2)	1.226 (20)
Rh(1)-N(7)	2.035 (15)	N(1)-O(3)	1.242 (21)
Rh(1)-P(1)	2.278 (6)	N(2)-C(62)	1.234 (21)
Rh(2)-O(1)	2.070 (14)	N(3)-C(62)	1.364 (21)
Rh(2)-O(2)	2.199 (16)	N(4)-C(61)	1.345 (20)
Rh(2)-N(2)	2.048 (16)	N(5)-C(61)	1.308 (22)
Rh(2)-N(5)	1.983 (15)	N(6)-C(66)	1.337 (19)
Rh(2)-N(6)	2.009 (16)	N(7)-C(66)	1.298 (20)
Bond Angles			
N(3)-Rh(1)-P(1)	93.1 (4)	N(2)-Rh(2)-O(1)	93.2 (6)
N(3)-Rh(1)-N(4)	87.5 (6)	N(2)-Rh(2)-O(2)	95.7 (6)
N(3)-Rh(1)-Rh(2)	88.4 (8)	N(2)-Rh(2)-Rh(1)	85.7 (5)
N(3)-Rh(1)-N(7)	171.9 (6)	N(2)-Rh(2)-N(5)	89.2 (6)
N(4)-Rh(1)-P(1)	172.8 (5)	N(2)-Rh(2)-N(6)	173.1 (7)
N(4)-Rh(1)-N(7)	86.4 (6)	N(5)-Rh(2)-O(1)	169.4 (6)
N(4)-Rh(1)-Rh(2)	86.9 (4)	N(5)-Rh(2)-O(2)	109.3 (6)
N(7)-Rh(1)-P(1)	93.6 (4)	N(5)-Rh(2)-Rh(1)	87.1 (5)
N(7)-Rh(1)-Rh(2)	86.0 (4)	N(5)-Rh(2)-N(6)	89.7 (6)
Rh(1)-N(3)-C(62)	116.7 (13)	N(6)-Rh(2)-O(1)	89.1 (6)
Rh(1)-N(7)-C(66)	121.9 (13)	N(6)-Rh(2)-O(2)	91.1 (6)
Rh(1)-Rh(2)-O(2)	163.6 (4)	N(6)-Rh(2)-Rh(1)	87.5 (4)
Rh(1)-Rh(2)-O(1)	103.4 (4)	Rh(2)-Rh(1)-P(1)	100.3 (2)
N(2)-C(62)-N(3)	124.3 (20)	Rh(2)-N(5)-C(61)	123.3 (14)
N(5)-C(61)-N(4)	120.8 (19)	Rh(2)-N(2)-C(62)	124.1 (15)
N(6)-C(66)-N(7)	121.9 (18)	Rh(2)-N(6)-C(66)	119.9 (14)
		O(2)-Rh(2)-O(1)	60.2 (5)

formation of the nearly stoichiometric amount of triphenylphosphine oxide. When the reaction is performed with a molar ratio less than 1:3, a corresponding amount of starting complex is recovered unreacted. This means that 2 equiv of PPh₃ are

sacrificed in the reduction of one nitrate group. Moreover, as the synthesis and workup of the complex **1** was carried out both in air as well as under a purified nitrogen atmosphere, we can exclude the possibility that the formation of 2 equiv of Ph₃PO is caused by air oxidation of the triphenylphosphine.

No further reaction of complex **1** was observed even when an excess of PPh₃ was used. Since steric factors probably do not influence the reactivity of the starting complex, we conclude that electronic effects are largely responsible for the lack of reductive elimination of the second nitrate group.

The analogous pyridine and dimethylamine complexes were synthesized by reacting Rh₂(form)₃(NO₃)₂ with an excess of pyridine and dimethylamine, respectively. Workup of the resulting solutions, as described in the Experimental Section, gave the air-stable complexes **2** and **3** in moderate yields. Although we have been unable to recover the amine oxides from the reaction mixtures, we suggest that eq 1 may be also applicable to the formation of **2** and **3**.

The complexes have been characterized by elemental analysis and IR spectroscopy and, for complex **2**, also by ¹⁰³Rh NMR spectroscopy and a single-crystal X-ray analysis. Molecular weights and magnetic susceptibilities measurements have been also determined in order to confirm the dimeric and diamagnetic nature of complexes **2** and **3**.

According to its crystal structure, the IR spectrum of complex **2** displays in the N=C=N stretching region only one strong absorption at 1580 cm⁻¹, pointing out the symmetric arrangement of the formamidinate groups around the Rh₂⁴⁺ core. On the basis of the IR data (ν(N=C=N) = 1585 cm⁻¹) a similar arrangement of the bridging ligands is also suggested for complex **3**. The ¹⁰³Rh NMR spectrum of **2**, although of poor quality because of sensitivity difficulties, is similar to that of **1**. It shows two signals at δ 6060 (d) and 4332 (d) assignable to two different rhodium nuclei.

Table III. Final Fractional Atomic Coordinates (×10⁴) for Non-Hydrogen Atoms of Rh₂(form)₃(NO₃)(PPh₃) (1)

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Rh(1)	2327 (1)	518 (1)	3129 (1)	C(17)	3298 (6)	751 (6)	-613 (13)
Rh(2)	2684 (1)	1503 (1)	3517 (2)	C(18)	2933 (6)	551 (6)	137 (13)
Cl(1)	-575 (19)	5284 (12)	2403 (25)	C(13)	2373 (6)	824 (6)	226 (13)
Cl(2)	-150 (25)	5248 (23)	4322 (56)	C(26)	1739 (6)	1976 (5)	5865 (14)
C(70)	-28 (30)	4857 (25)	3422 (56)	C(27)	1647 (6)	2414 (5)	6851 (14)
N(1)	2585 (10)	2372 (9)	2335 (20)	C(28)	1561 (6)	2955 (5)	6150 (14)
O(1)	2338 (6)	1901 (6)	1974 (12)	C(29)	1568 (6)	3059 (5)	5003 (14)
O(2)	2872 (8)	2396 (7)	3335 (15)	C(30)	1661 (6)	2621 (5)	4288 (14)
O(3)	2519 (8)	2785 (7)	1694 (16)	C(25)	1746 (6)	2079 (5)	4719 (14)
C(63)	4124 (11)	-1820 (8)	4149 (22)	C(32)	3444 (5)	2139 (6)	5861 (11)
C(64)	-784 (9)	-564 (9)	3187 (21)	C(33)	3881 (5)	2469 (6)	6609 (11)
C(65)	4903 (10)	2569 (10)	8124 (19)	C(34)	4434 (5)	2231 (6)	7252 (11)
C(67)	5021 (12)	2994 (10)	1636 (26)	C(35)	4549 (5)	1663 (6)	7153 (11)
C(68)	1804 (14)	-1613 (10)	6565 (20)	C(36)	4112 (5)	1333 (6)	6412 (11)
C(69)	1405 (16)	3425 (12)	6858 (30)	C(31)	3560 (5)	1571 (6)	5770 (11)
N(2)	1855 (8)	1611 (7)	4073 (14)	C(38)	4325 (8)	1986 (7)	3461 (11)
C(62)	1433 (10)	1255 (9)	3982 (17)	C(37)	3873 (8)	1707 (7)	2645 (11)
N(3)	1469 (7)	736 (6)	3536 (13)	C(39)	4700 (8)	2401 (7)	3121 (11)
N(4)	2661 (7)	373 (6)	4819 (14)	C(40)	4623 (8)	2537 (7)	1965 (11)
C(61)	3012 (9)	760 (9)	5483 (18)	C(41)	4171 (8)	2258 (7)	1148 (11)
N(5)	3100 (7)	1253 (7)	5077 (14)	C(42)	3796 (8)	1843 (7)	1488 (11)
N(6)	3471 (7)	1299 (6)	2954 (13)	C(44)	3252 (5)	-613 (6)	2485 (9)
C(66)	3626 (9)	763 (8)	2875 (16)	C(45)	3466 (5)	-1151 (6)	2802 (9)
N(7)	3228 (7)	363 (6)	2930 (13)	C(46)	3949 (5)	-1232 (6)	3768 (9)
P(1)	1924 (3)	563 (2)	1209 (5)	C(47)	4218 (5)	-775 (6)	4417 (9)
C(2)	1660 (6)	-509 (6)	1706 (10)	C(48)	4003 (5)	-238 (6)	4100 (9)
C(3)	1648 (6)	-1087 (6)	1577 (10)	C(43)	3520 (5)	-157 (6)	3134 (9)
C(4)	1797 (6)	-1327 (6)	602 (10)	C(50)	2274 (6)	-112 (5)	6359 (11)
C(5)	1958 (6)	-989 (6)	-244 (10)	C(51)	2053 (6)	-603 (5)	6768 (11)
C(6)	1971 (6)	-411 (6)	-115 (10)	C(52)	2063 (6)	-1100 (5)	6167 (11)
C(1)	1822 (6)	-171 (6)	860 (10)	C(53)	2292 (6)	-1108 (5)	5159 (11)
C(8)	1035 (6)	1394 (6)	1047 (10)	C(54)	2513 (6)	-617 (5)	4751 (11)
C(9)	442 (6)	1637 (6)	632 (10)	C(49)	2504 (6)	-119 (5)	5351 (11)
C(10)	-25 (6)	1343 (6)	-125 (10)	C(56)	934 (5)	-113 (6)	3935 (11)
C(11)	99 (6)	806 (6)	-466 (10)	C(57)	382 (5)	-428 (6)	3860 (11)
C(12)	691 (6)	563 (6)	-51 (10)	C(58)	-200 (5)	-218 (6)	3273 (11)
C(7)	1159 (6)	857 (6)	706 (10)	C(59)	-230 (5)	307 (6)	2760 (11)
C(14)	2179 (6)	1297 (6)	-435 (13)	C(60)	323 (5)	621 (6)	2835 (11)
C(15)	2544 (6)	1497 (6)	-1184 (13)	C(55)	904 (5)	411 (6)	3423 (11)
C(16)	3104 (6)	1224 (6)	-1273 (13)				

Table IV. Selected Bond Lengths (Å) and Angles (deg) for $\text{Rh}_2(\text{form})_3(\text{NO}_3)(\text{C}_5\text{H}_5\text{N})$ (2)

Bond Distances			
Rh(1)–Rh(2)	2.476 (1)	N(3)–C(62)	1.319 (11)
Rh(1)–N(8)	2.089 (7)	N(3)–C(55)	1.436 (10)
Rh(1)–N(5)	2.021 (7)	N(4)–C(61)	1.314 (10)
Rh(1)–N(2)	2.053 (6)	N(4)–C(49)	1.421 (11)
Rh(1)–N(6)	2.060 (6)	N(5)–C(31)	1.440 (10)
Rh(2)–O(1)	2.286 (6)	N(5)–C(61)	1.311 (11)
Rh(2)–O(2)	2.118 (6)	N(6)–C(37)	1.404 (11)
Rh(2)–N(4)	2.010 (7)	N(6)–C(63)	1.345 (10)
Rh(2)–N(3)	2.082 (6)	N(7)–C(43)	1.443 (9)
Rh(2)–N(7)	2.036 (6)	N(7)–C(63)	1.299 (11)
N(1)–O(3)	1.210 (10)	O(2)–N(1)	1.286 (10)
N(2)–C(26)	1.428 (11)	O(1)–N(1)	1.274 (11)
N(2)–C(62)	1.341 (12)		
Bond Angles			
N(5)–Rh(1)–N(6)	90.2 (2)	N(2)–Rh(1)–N(6)	173.5 (3)
N(2)–Rh(1)–N(5)	89.0 (3)	N(8)–Rh(1)–N(6)	89.4 (3)
N(8)–Rh(1)–N(5)	179.2 (2)	N(8)–Rh(1)–N(2)	91.5 (3)
Rh(2)–Rh(1)–N(6)	87.3 (2)	Rh(2)–Rh(1)–N(5)	86.3 (2)
Rh(2)–Rh(1)–N(2)	86.2 (2)	Rh(2)–Rh(1)–N(8)	94.3 (2)
Rh(1)–Rh(2)–N(7)	84.9 (2)	Rh(1)–Rh(2)–N(4)	85.6 (2)
Rh(1)–Rh(2)–N(3)	86.7 (2)	Rh(1)–Rh(2)–O(2)	101.9 (2)
N(4)–Rh(2)–N(7)	90.3 (2)	N(3)–Rh(2)–N(7)	171.7 (2)
N(3)–Rh(2)–N(4)	88.8 (2)	O(2)–Rh(2)–N(7)	92.5 (2)
O(2)–Rh(2)–N(4)	172.1 (2)	O(2)–Rh(2)–N(3)	89.5 (2)
O(1)–Rh(1)–N(7)	92.0 (2)	O(1)–Rh(1)–N(4)	113.8 (2)
O(1)–Rh(1)–N(3)	96.0 (2)	O(1)–Rh(1)–O(2)	58.8 (2)
O(2)–N(1)–O(3)	122.5 (9)	O(1)–N(1)–O(3)	122.2 (9)
O(1)–N(1)–O(2)	115.2 (8)	Rh(1)–N(8)–C(5)	121.5 (5)
Rh(1)–N(8)–C(1)	121.8 (5)	Rh(1)–N(2)–C(62)	118.3 (6)
N(2)–C(62)–N(3)	123.6 (8)	Rh(2)–N(3)–C(62)	117.1 (6)
N(4)–C(61)–N(5)	123.2 (8)	Rh(1)–N(5)–C(61)	118.3 (5)
Rh(1)–N(6)–C(63)	116.0 (5)	N(6)–C(63)–N(7)	123.0 (7)
Rh(2)–N(7)–C(63)	120.5 (5)		

Figure 2 illustrates the molecular structure of complex **1** and the atomic labeling scheme. Selected bond distances and angles are shown in Table II; the final fractional atomic coordinates are given in Table III. The crystal structure consists of an unsymmetrical dirhodium unit bridged by three formamidinate ligands. One triphenylphosphine group completes the coordination sphere around Rh(1), which adopts a pseudo-square-pyramidal geometry. The stereochemistry of the Rh(2) is pseudooctahedral owing to the unsymmetrically coordinated nitrate group. The Rh–Rh bond distance of 2.498 (2) Å is considerably longer than the distances found in most of the Rh_2^{4+} derivatives,⁴ where the two metal centers are spanned by four bridging ligands. It is comparable with the values of 2.485 (1) Å found in the parent complex $\text{Rh}_2(\text{form})_3(\text{NO}_3)_2$ ^{2a} where the same number of formamidinate groups is present. It is worthwhile mentioning that as the average formal oxidation state decreases from 2.5 to 2 the Rh–Rh separation increases by 0.013 Å. The length of the Rh–P bond [2.278 (6) Å] is comparable with the values reported for Rh_2^{4+} derivatives where the phosphorus occupies an equatorial position.^{5b,13}

The deviation from the idealized geometry around Rh(1) [$\text{Rh}(2)\text{--Rh}(1)\text{--P}(1) = 100.3(2)^\circ$] is probably due to the steric overcrowding of the phenyl rings of the triphenylphosphine and the *p*-tolyl groups. The consequent repulsive contacts push one phenyl group toward the axial position. The long-range interactions that can be postulated on the basis of the $\text{Rh}(1)\cdots\text{C}(1)$ (3.164 Å) and $\text{Rh}(1)\cdots\text{C}(55)$ (3.166 Å) separations prohibit any kind of axial coordination. The bond lengths and angles within the N(4)–C(61)–N(5) and N(6)–C(66)–N(7) fragments are similar to those found in the parent complex and are indicative of extensive electronic delocalization. The remaining bridging group is arranged in an unusual fashion: the N(2)–C(62) and

Table V. Final Fractional Atomic Coordinates ($\times 10^4$) for Non-Hydrogen Atoms of $\text{Rh}_2(\text{form})_3(\text{NO}_3)(\text{C}_5\text{H}_5\text{N})$ (2)

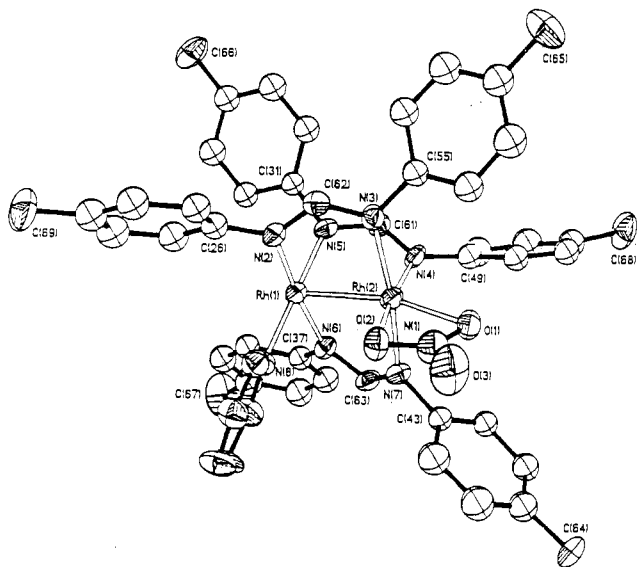
atom	<i>x/a</i>	<i>xb</i>	<i>z/c</i>
Rh(1)	2168 (1)	–2514 (1)	3950 (1)
Rh(2)	1620 (1)	–1412 (1)	3375 (1)
N(1)	1507 (8)	–1381 (6)	2456 (3)
O(1)	1143 (5)	–758 (4)	2672 (2)
O(2)	1853 (6)	–1987 (4)	2722 (2)
O(3)	1527 (8)	–1397 (5)	2030 (2)
N(8)	1730 (7)	–3433 (4)	3456 (2)
C(1)	2422 (8)	–3533 (3)	3079 (3)
C(2)	2138 (9)	–4122 (6)	2746 (3)
C(3)	1129 (10)	–4643 (6)	2790 (3)
C(4)	407 (9)	–4555 (6)	3171 (4)
C(5)	719 (9)	–3949 (6)	3494 (3)
N(2)	4051 (6)	–2422 (5)	3764 (2)
C(62)	4433 (8)	–1717 (6)	3589 (3)
N(3)	3612 (6)	–1133 (4)	3446 (2)
N(4)	1406 (6)	–722 (4)	3946 (2)
C(61)	2082 (8)	–915 (5)	4348 (3)
N(5)	2581 (6)	–1634 (4)	4436 (2)
N(6)	229 (5)	–2497 (4)	4088 (2)
C(63)	–625 (7)	–2196 (5)	3742 (3)
N(7)	–260 (6)	–1811 (4)	3378 (2)
C(26)	4940 (8)	–3087 (5)	3819 (3)
C(27)	5921 (9)	–3196 (5)	3514 (3)
C(28)	6695 (9)	–3885 (6)	3571 (3)
C(29)	6554 (9)	–4454 (6)	3917 (3)
C(69)	7400 (10)	–5209 (7)	3975 (4)
C(30)	5589 (10)	–4337 (6)	4214 (4)
C(25)	4781 (9)	–3649 (6)	4163 (3)
C(31)	3603 (8)	–1711 (5)	4820 (3)
C(32)	4597 (8)	–1146 (5)	4899 (3)
C(33)	5579 (8)	–1253 (6)	5273 (3)
C(34)	5602 (9)	–1903 (6)	5562 (3)
C(66)	6722 (9)	–2008 (7)	5962 (3)
C(35)	4639 (8)	–2489 (6)	5484 (3)
C(36)	3621 (8)	–2377 (5)	5111 (3)
C(37)	–272 (8)	–2877 (5)	4474 (3)
C(38)	–1480 (8)	–2675 (5)	4633 (3)
C(39)	–1987 (10)	–3127 (6)	4986 (3)
C(40)	–1282 (9)	–3747 (6)	5211 (4)
C(67)	–1851 (14)	–4248 (8)	5602 (5)
C(41)	–64 (9)	–3922 (5)	5072 (3)
C(42)	428 (8)	–3494 (5)	4707 (3)
C(43)	–1302 (7)	–1619 (5)	3016 (3)
C(44)	–1348 (9)	–2023 (6)	2576 (4)
C(45)	–2345 (10)	–1818 (7)	2214 (4)
C(46)	–3279 (9)	–1242 (6)	2289 (3)
C(64)	–4288 (10)	–984 (7)	1887 (4)
C(47)	–3219 (8)	–865 (5)	2716 (3)
C(48)	–2225 (8)	–1044 (5)	3078 (3)
C(49)	680 (8)	10 (5)	3926 (3)
C(50)	60 (9)	267 (6)	4315 (3)
C(51)	–503 (10)	1030 (6)	4323 (4)
C(52)	–518 (9)	1539 (6)	3941 (3)
C(68)	–1055 (11)	2397 (6)	3974 (4)
C(53)	15 (8)	1257 (5)	3542 (3)
C(54)	611 (8)	514 (5)	3537 (3)
C(55)	4175 (8)	–356 (5)	3368 (3)
C(56)	3738 (8)	113 (6)	2992 (3)
C(57)	4313 (9)	855 (6)	2913 (3)
C(58)	5343 (9)	1136 (6)	3212 (3)
C(65)	5960 (11)	1961 (6)	3116 (4)
C(59)	5783 (9)	666 (6)	3587 (3)
C(60)	5219 (8)	–60 (5)	3680 (3)

N(3)–C(62) bond distances are 1.234 (21) and 1.364 (21) Å, respectively. In particular the former distance lies in the range quoted for isolated C=N double bonds, indicating reduced electronic delocalization within the N(2)–C(62)–N(3) skeletal system. Therefore the bonding description of the third formamidinate group is consistent with a Rh(1)–N(3) σ -bond via the amino nitrogen N(3) and a dative Rh(2)–N(2) bond via the imino nitrogen N(2). A formamidinate anion bonded to the metal center via the amino nitrogen has been recently reported for the mononuclear complex $[\text{Pt}(\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6})(\text{dptf})]$ (dptf = *p*-MeC₆H₄N=CHNC₆H₄Me-*p*) even if the C–N(amino) and

(13) (a) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A.; Tocher, J. H. *Organometallics* **1985**, *4*, 8. (b) Barcelo, F.; Cotton, F. A.; Lahuerta, P.; Llusar, R.; Sanau, M.; Schwotzer, W.; Ubeda, M. A. *Ibid.* **1986**, *5*, 808. (c) Barcelo, F.; Lahuerta, P.; Ubeda, M. A.; Foces-Foces, C.; Cano, F. H.; Martinez-Ripoll, M. J. *Chem. Soc., Chem. Commun.* **1985**, 43. (d) Cotton, F. A.; Dumbur, K. R.; Verbruggen, M. G. *J. Am. Chem. Soc.* **1987**, *109*, 5498.

Table VI. Selected Bond Distances (Å) and Angles (deg) for Rh₂(form)₃(NO₃)(PPh₃) (**1**), Rh₂(form)₃(NO₃)(C₅H₅N) (**2**), Rh₂(form)₃(NO₃)₂ (**3**), Rh₂(form)₄ (**4**), and Rh₂(form)₂(O₂CCF₃)₂(H₂O)₂ (**5**)

	1	2	3	4	5
Rh-Rh	2.498 (2)	2.476 (1)	2.485 (1)	2.4336 (4)	2.425 (1)
Rh-O(equat)	2.070	2.118 (6)	2.080		2.083
			2.086		
Rh-O(axial)	2.199	2.280 (6)	2.382		2.315
			2.287		
N-C	1.322	1.321	1.324	1.331 (5)	1.308
N-C-N	122.4	123.3	123	123.7 (8)	124.6
Rh-Rh-O(equat)	104.5	101.9	95.6		
			99.0		
Rh-Rh-O(axial)	163.7	160.4	151.9		168.2
			156.2		
N-Rh-Rh-N	8.8	20.8	6.8	16.7 (2)	9.4
X-Rh-Rh-Y	7.2	23.3	5.1		8.1

**Figure 3.** Molecular structure and atom-labeling scheme for Rh₂(form)₃(NO₃)(C₅H₅N) (**2**).

C-N(imino) bond distances are 1.345 (8) and 1.303 (7) Å, respectively.¹

Figure 3 illustrates the molecular structure of **2** with the atomic labels; selected bond distances and angles and some relevant torsional angles are reported in Table IV, the final atomic coordinates are given in Table V. The coordination structure of the two rhodium atoms in **2** is very similar to that in **1**. The Rh(1)-Rh(2) bond distance [2.476 (1) Å] is 0.009 Å shorter with respect to that in the parent complex in spite of the lower bond order. The length of the Rh(1)-N(8) bond [2.089 (7) Å] compares with the Rh-N bond distances of the formamidinate groups in trans position to each other. These distances range from 2.036 (6) to 2.082 (6) Å and are in line with the values reported for Rh-N(equat)¹⁴ bond distances whereas longer distances have been reported for Rh-N(axial) bonds.¹⁵

Steric interactions between the pyridine and the *p*-tolyl groups, although less important than in the triphenylphosphine derivative, may explain the value of the Rh(2)-Rh(1)-N(8) angle [94.3 (2)] as well as the twisting of the pyridine ring with respect to the Rh-Rh basal plane [Rh(2)-Rh(1)-N(8)-C(1) = 64.2 (6)°].

The values of the N(8)-Rh(1)-Rh(2)-O(2) [-23.3 (2)°] and N-Rh-Rh-N torsion angles [mean value -20.8 (3)°] lie close to the values found in the complexes Rh₂(form)₄^{2c}, Rh₂(benzamidinate)₄,¹⁶ and M₂(form)₄ (M = Ni, Pd).¹⁷ The O(1)-Rh-

(1)-Rh(2)-P(1) and N-Rh-Rh-N torsion angles in **1** are 7.2 (3) and 8.7 (4)°, respectively. Similar values were also found in the complexes Rh₂(form)₃(NO₃)₂^{2b} and Rh₂(form)₂(O₂CCF₃)₂(H₂O)₂, as shown in Table VI, where are reported, for comparison, the structural data of a series of formamidinate derivatives. Intramolecular steric interactions and crystal-packing forces may be invoked, as usual, to explain the torsional conformation of the above-cited complexes.

The Rh-O(equat) bond distances of **1** [2.070 (14) Å] and **2** [2.118 (6) Å] are shorter than the corresponding Rh-O(axial) distances [2.199 (10) Å for **1** and 2.280 (6) Å for **2**] as a consequence of the trans influence of the Rh-Rh bond. The Rh-O(axial) bond distance in **2** is longer than the corresponding values found in complex **1**. Such results may be explained considering the Rh-Rh-O(axial) bond angles; the longest Rh-O(axial) bond distances are associated with the greatest deviation of the Rh-Rh-O(axial) angle from the linearity.

In the N-C-N fragments the N...N separation ranges from 2.310 to 2.344 Å while bond lengths [mean value N-C = 1.321 (10) Å] and N-C-N angles are, as found in the complexes cited in Table VI, indicative of extensive electronic delocalization.

Concluding Remarks

The Rh₂⁵⁺ complex Rh₂(form)₃(NO₃)₂ reacts with an excess of PPh₃, pyridine, and dimethylamine giving the Rh₂⁴⁺ derivatives **1**, **2**, and **3**. The comparison of the X-ray structural data of the complexes **1** and **2** reveals, in addition to the 0.022-Å difference in the Rh-Rh bond distances, a significant difference in the bonding mode of one bridging group. The bonding description of one formamidinate group of complex **1** can be best described as σ,σ-N,N' with a localized double bond. On the contrary, the three formamidinate groups of complex **2** are bridged to the dirhodium unit in the usual way, namely σ,σ-N,N' with delocalized double bonds. This fact makes the compounds very intriguing from the metal-metal interaction point of view. This can be regarded as a donor-acceptor metal-metal bond if the six-coordinate Rh(2) and the five-coordinate Rh(1) are assigned the formal oxidation states of 3 and 1, respectively, according to the description given by Cotton for the complex (COD)Ir(μ-form)₂(O₂CCF₃)₂(H₂O).¹⁸ Alternatively, it can be regarded as a covalent metal-metal bond if both the rhodium atoms exhibit oxidation state 2; nonintegral oxidation states are also possible. Owing to the different coordination geometry of one of the formamidinate groups, the Rh(1) and consequently the Rh(2) atom of complex **1** exhibit very likely different formal oxidation states with respect to the Rh(1) atoms of the complexes **2** and **3** (the IR spectrum of complex **3** shows only one N-C-N stretching band, supporting the suggestion that the formamidinate groups are symmetrically bridged to the dimetal center). On the basis of the available data, we cannot unambiguously assign formal oxidation numbers to the rhodium atoms of complexes **1**, **2**, and **3**; however, we think that complex **1**, despite the different coordination of the two rhodium atoms, may be described as a homo-

(14) (a) Baker, A. T.; Tikkanen, W. R.; Kaska, W. C.; Ford, P. C. *Inorg. Chem.* **1984**, *23*, 3254. (b) Barron, A. R.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *Polyhedron* **1985**, *4*, 1131. (c) Ahsan, M. Q.; Bernal, I.; Bear, J. L. *Inorg. Chem.* **1986**, *25*, 260.

(15) Farrel, N.; Vargas, M. D.; Mascarenhas, Y. A.; Gambardella, M. P. *Inorg. Chem.* **1987**, *26*, 1426 and references therein.

(16) Le, J. C.; Chavan, M. Y.; Chau, L. K.; Bear, J. L.; Kadish, K. M. *J. Am. Chem. Soc.* **1985**, *107*, 7195.

(17) Cotton, F. A.; Matusz, M.; Poli, R. *Inorg. Chem.* **1987**, *26*, 1472.

(18) Cotton, F. A.; Poli, R. *Inorg. Chem.* **1987**, *26*, 590.

geneous-valence Rh_2^{4+} dimer whereas complexes **2** and **3** are best described as mixed-valence complexes with nonintegral oxidation states.

Acknowledgment. We thank Dr. B. E. Mann (University of Sheffield) for the ^{103}Rh NMR spectra and the Public Ministry of Education for financial support.

Registry No. **1**, 117369-58-1; **2**, 117340-66-6; **3**, 117340-67-7; $\text{Rh}_2(\text{form})_3(\text{NO}_3)_2$, 99416-57-6; Rh, 7440-16-6.

Supplementary Material Available: Tables SI-SVI, listing atomic distances and angles associated with the tolyl, phenyl, and nitrate groups, hydrogen atom parameters, and temperature factors (10 pages); tables of calculated and observed structure factors (32 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3, Canada

$p\pi-p\pi$ Bonding between Phosphorus and Sulfur: Synthesis and Characterization of a Dithiophospholium Cation¹

Neil Burford,* Bruce W. Royan,² Anthony Linden, and T. Stanley Cameron[†]

Received May 20, 1988

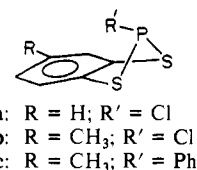
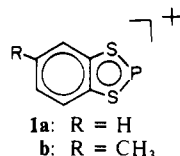
Salts of the first dithiophospholium cation have been isolated and fully characterized as aromatic derivatives. The synthesis involves a chloride ion abstraction in CH_2Cl_2 . The competitive aromatic electrophilic substitution is avoided by the use of high dilution conditions. An X-ray crystal structure of 1,3,2-benzodithiophospholium (**1a**) tetrachloroaluminate indicates a planar geometry for the cation with short P-S bonds (mean 2.016 (2) Å) and short C-S bonds (mean 1.719 (4) Å). Crystal data for $\text{C}_6\text{H}_4\text{S}_2\text{PAlCl}_4$: monoclinic, space group $P2_1/c$, $a = 6.605$ (3) Å, $b = 23.377$ (4) Å, $c = 8.666$ (2) Å, $\beta = 100.28$ (3)°, $V = 1316.5$ Å³, $Z = 4$, $R = 0.036$. The spectroscopic and structural data are interpreted in terms of unique $3p\pi-3p\pi$ bonding across the S-P-S moiety. This is highlighted by the crystal structure of the P-S σ -bonded 5-methyl-2-phenyl-1,3,2-benzodithiophosphole (**2c**), which has P-S bonds of 2.110 (2) and 2.102 (2) Å. Crystal data for $\text{C}_{13}\text{H}_{11}\text{S}_2\text{P}$: monoclinic, space group $P2_1/n$, $a = 14.691$ (3) Å, $b = 6.291$ (1) Å, $c = 14.882$ (3) Å, $\beta = 114.56$ (2)°, $V = 1250.9$ Å³, $Z = 4$, $R = 0.037$. The new cation contains the first example of thermodynamically stable $p\pi-p\pi$ bonding between phosphorus and sulfur and, in addition, a rare example of $p\pi-p\pi$ bonding between the heavier elements of different groups of the periodic table. The stabilizing features of charge and aromatic π -electron count offer great generality and indicate the potential for the formation of an extensive series of compounds containing $p\pi-p\pi$ bonding between the heavier non-metal elements.

Introduction

The π -bond is often the origin of diverse and exciting chemistry. However, very few elements are observed to employ general stable $p\pi$ -bonding.³ Kutzelnigg has suggested that weak $p\pi$ -bonding is standard for the non-metals and that the very strong $p\pi$ -bonds observed for carbon, nitrogen, and oxygen are anomalous.⁴ Nevertheless, examples of compounds containing stable $p\pi$ -bonding between the heavier non-metal elements have been prepared and fully characterized. On this basis, Schmidt and Gordon have predicted that "Eventually compounds representing all possible double bonds between atoms of groups 14-16 will be isolated and characterized", and have provided useful theoretical π -bond strengths between many non-metal elements.⁵

Despite the thermodynamic preference for σ -bonding over π -bonding exhibited by most non-metal elements, specific structural or electronic features have been used to stabilize systems employing $(np-np)\pi$ bonding, where $n > 2$. However, the imposition of these features is restricted and is dependent upon the fundamental periodic chemical properties of the elements involved. For example, $p\pi$ -bonds between the heavier elements of groups 14 and 15 can be kinetically stabilized by the steric constraints of bulky substituent groups.⁶ Such arrangements are not possible for elements of groups 16 and 17 due to the greater number of valence electrons. Instead, $p\pi$ -bonding between the chalcogens and halogens can be induced by the presence of a molecular positive charge,^{7,8} a feature that has not yet been exploited for the elements of groups 14 and 15. Consequently, experimental evidence for $p\pi-p\pi$ bonding between the heavier elements ($n > 2$) from opposite sides of the p-block is not available. In an attempt to develop more general non-metal $p\pi$ -bonding, we describe the synthesis and spectroscopic characterization of the first dithiophospholium cation, which contains a unique example of thermodynamically stable $3p\pi-3p\pi$ bonding between phosphorus and sulfur. The crystal structure of 1,3,2-benzodithiophospholium (**1a**)

tetrachloroaluminate is presented as supportive evidence for a delocalized $p\pi$ -structure. A direct comparison with a fully σ -bonded system is discussed on the basis of the crystal structure of the derivative parent phosphine, 5-methyl-2-phenyl-1,3,2-benzodithiophosphole (**2c**).



Experimental Section

General Procedures. CH_2Cl_2 , CHCl_3 , CD_2Cl_2 , and CDCl_3 were dried over P_2O_5 and stored over CaH_2 . For some NMR samples the solvent was also predried by storage over samples of the compounds under study.

- (1) For a preliminary communication of this work see: Burford, N.; Royan, B. W.; Linden, A.; Cameron, T. S. *J. Chem. Soc., Chem. Commun.* **1988**, 842.
- (2) I. W. Killam Memorial Graduate Scholarship.
- (3) See, for example: Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: New York, 1984.
- (4) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, 23, 272.
- (5) Schmidt, M. W.; Truong, P. N.; Gordon, M. S. *J. Am. Chem. Soc.* **1987**, 109, 5217.
- (6) See, for example: (a) Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268. (b) West, R.; Fink, M. J.; Michl, J. *Science (Washington, D.C.)* **1981**, 214, 1343. (c) Yoshifugi, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, 103, 4587. (d) Masamune, S.; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *Ibid.* **1982**, 104, 1150. (e) Cowley, A. H.; Kilduff, J. E.; Newman, T. H.; Pakulski, M. *Ibid.* **1982**, 104, 5820. (f) Escudie, J.; Couret, C.; Satge, J.; Andrianarison, M.; Andriamizaka, J.-D. *Ibid.* **1985**, 107, 3378. (g) Couret, C.; Escudie, J.; Satge, J.; Rahannirina, A.; Andriamizaka, J.-D. *Ibid.* **1985**, 107, 8280. (h) Drager, M.; Escudie, J.; Couret, C.; Ranivonjatova, H.; Satge, J. *Organometallics* **1988**, 7, 1010.
- (7) (a) Gillespie, R. J. *Chem. Soc. Rev.* **1979**, 8, 315. (b) Gillespie, R. J.; Passmore, J. *Adv. Inorg. Chem. Radiochem.* **1975**, 17, 49, and references therein.
- (8) Burford, N.; Passmore, J.; Sanders, J. P. *Molecular Structure and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH: Weinheim, FRG; in press; and references therein.

* To whom correspondence should be addressed.

[†] X-ray structural determinations.