

is also of interest to note that the long Fe1-S2 distance of 2.238 (5) Å is accompanied by a short S2-C8 distance of 1.721 (18) Å, in contrast to the corresponding values of 2.160 (5) (Fe1-S1) and 1.782 (18) Å (S1-C1). The two intact S-S bond lengths in **1** are 2.077 (8) Å (S3-S4) and 2.086 (8) Å (S5-S6).

The structure of **2** (Figure 2) or **3** (Figure 3) can be described as two $M(\eta^5\text{-C}_5\text{H}_5)$ moieties bridged by two sulfur atoms (S1 and S2) (in a butterfly-like arrangement) from one end of the TCTTN ligand via oxidative addition, leaving the other S3-S4 bond intact at ca. 2.07 Å. There is a single Co-Co bond of 2.415 (3) (molecule A) or 2.434 (3) Å (molecule B) in **2** but nonbonding Ni...Ni contacts at 2.951 (3) (molecule A) or 2.809 (3) Å (molecule B) in **3**, in accord with the noble gas rule. The average Co-Co distance of 2.425 Å in **2** is among the shortest single cobalt-cobalt bonds known (e.g., $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2(\text{PPh}_2)_2$,¹² 2.56 (1) Å; $\text{Co}_2(\text{CO})_6(\text{C}_2(\text{t-Bu})_2)$,¹³ 2.463 (1) Å). The average Ni...Ni distance of 2.880 Å is among the shortest nonbonding nickel...nickel distances known (e.g., $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}_2(\text{PPh}_2)_2$,¹² 3.36 (1) Å). In fact, it is even 0.26 Å shorter than the metal-metal distance of 3.14 Å in $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\text{PPh}_2)_2]^+$ with a formal bond order of $1/2$.³ The soft Ni...Ni interaction is probably responsible for the 0.14 Å difference in the Ni...Ni distance between the two independent molecules in the unit cell. The stereochemical contrast between **2** and **3** on the one hand and $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}_2(\text{PPh}_2)_2$ where M = Co and Ni on the other is rather interesting.

It is interesting to compare the dihedral angle (angle between the normals) between the two MS_2 planes within the butterfly-like M_2S_2 fragment in **2** and **3**. The values are 78.6° and 77.2° for **2** and 44.1° and 54.5° for **3** for molecules A and B, respectively. Apparently, the addition of two electrons to the metal-metal antibonding orbital (presumed to be the lowest unoccupied molecular orbital)¹⁴ in the dicobalt species to form the dinickel cluster is responsible for the opening of the M_2S_2 fragment and the drastic change in the dihedral angle of ca. 30°. Furthermore, while the dihedral angle formed by the C_3S_2 plane and the MS_2 plane in all the structurally characterized metal tetrathiolene complexes¹ generally fall in the range of 38.9-52.8°, the values are 50.4-51.8° in **2** and 62.6-68.0° in **3**. We note that the observed Ni...Ni distance of 2.880 Å in **3** is not far from the limiting distance of 3.184 (molecule A) or 3.159 Å (molecule B) at the extreme dihedral angle of 90° between the C_3S_2 and MS_2 planes (or 0° between the two MS_2 planes).

It is conceivable that the sought-after Fe=Fe double bond, presumably formed in the early stage(s) of the reaction of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$ with TCTTN, is so reactive that it further reacts with TCTTN with the unexpected elimination of one sulfur to form **1**.^{15,16} At least one other major product in the filtrate of the reaction has been identified by HPLC.¹⁷ Characterization (in progress) of this or other reaction products will eventually provide evidence for the fate of the "lost" sulfur atom as well as shed light on the desulfurization process. Nevertheless, the present study represents a new example of desulfurization of aryl disulfides (and the first example for the tetrathiolene ligands) under very mild conditions (at atmospheric pressure, low temperature, and in the absence of hydrogen).^{18,19}

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(18) For other stoichiometric desulfurization reactions, see the work of Alper,²⁰ Kaesz,²¹ Gilman,²² Weiss,²³ Dilworth,²⁴ Eisch,²⁵ and others.

(19) It is interesting to note that most industrial processes for the removal of organic sulfur from petroleum or coal or as a pollutant involves hydrodesulfurization at high temperature (350-450 °C) and high pressure (33-165 atm) in the presence of catalysts such as presulfidated cobalt-molybdena or nickel-tungsten supported on alumina.²⁶⁻³⁶

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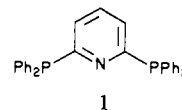
Phosphine Ligands for the Construction of Polynuclear Complexes. 2. 2,6-Bis(diphenylphosphino)pyridine Complexes of Palladium(II) and Rhodium(I)

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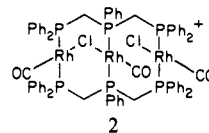
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As part of our studies^{1,2} exploring the use of polyfunctional phosphine ligands for the construction of multinuclear transition-metal complexes, we have examined the coordination behavior of 2,6-bis(diphenylphosphino)pyridine (**1**) ($(\text{Ph}_2\text{P})_2\text{py}$).³ In this



paper we compare and contrast the binding of two d⁸ metal ions, Pd(II) and Rh(I) with **1** and the related triphosphine bis(diphenylmethyl)phenylphosphine (dpmp). The latter forms a simple, chelated complex, (dpmp)PdCl₂, with palladium and a remarkable trinuclear complex, **2**, with rhodium.



The ligand $(\text{Ph}_2\text{P})_2\text{py}$ is closely related to 2-(diphenylphosphino)pyridine (Ph_2Ppy), which has been useful in constructing binuclear, particularly heterobinuclear, complexes.³ Because of the location of the pyridine ring, $(\text{Ph}_2\text{P})_2\text{py}$ is con-

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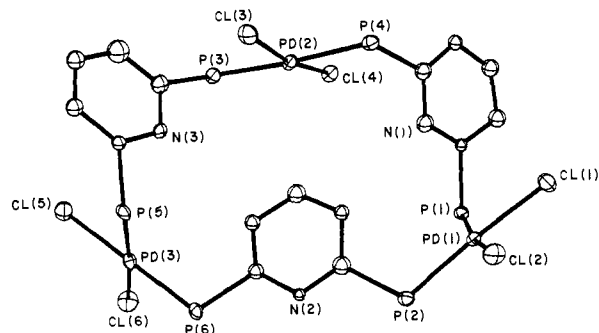
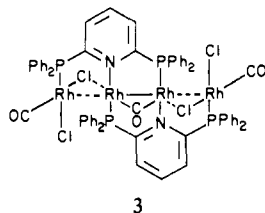


Figure 1. A perspective drawing of the structure of $[\mu-(\text{Ph}_2\text{P})_2\text{py}]_3\text{Pd}_3\text{Cl}_6$. In order to clarify the drawing, the two phenyl groups on each phosphorus atom have been omitted.

siderably less flexible than dpmp. As a result, $(\text{Ph}_2\text{P})_2\text{py}$ cannot function as a chelating diphosphine, although chelation through a P and N donor pair, as found for Ph_2Ppy ,⁴ is a possibility. The limited flexibility is demonstrated in the reaction of $(\text{Ph}_2\text{P})_2\text{py}$ with Pd(II). (1,5-Cyclooctadiene)palladium(II) chloride reacts with $(\text{Ph}_2\text{P})_2\text{py}$ in dichloromethane to give a yellow solution from which pale yellow $[\mu-(\text{Ph}_2\text{P})_2\text{py}]_3\text{Pd}_3\text{Cl}_6$ is crystallized in 76% yield upon the addition of ethyl ether. The structure of the interior, nonplanar, 18-membered ring of trinuclear complex, as revealed by an X-ray crystallographic structure determination, is shown in Figure 1.⁵ The molecule possesses no symmetry. Two of the palladium ions are bound by cis pairs of chloride ions and phosphorus atoms, while the remaining palladium is bonded to trans pairs of chloride and phosphorus. The nitrogen atoms are uncoordinated. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\mu-(\text{Ph}_2\text{P})_2\text{py}]_3\text{Pd}_3\text{Cl}_6$ in dichloromethane solution consists of three equally intense resonances at 37.8, 23.0, and 17.0 ppm (reference, external 85% H_3PO_4). Consequently, it appears that the trinuclear structure is retained in solution, although conformational flexibility renders the following pairs of phosphorus atoms equivalent: P(1) and P(5), P(2) and P(6), and P(3) and P(4). The cyclic structure is quite stable with respect to other isomers and differing degrees of polymerization. After heating at 132 °C for 5 days, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a sample of $[\mu-(\text{Ph}_2\text{P})_2\text{py}]_3\text{Pd}_3\text{Cl}_6$ in chlorobenzene solution is unchanged.

A very different, tetranuclear complex is formed from this ligand and rhodium(I). Heating a benzene solution containing equimolar amounts of dicarbonylrhodium(I) chloride dimer and $(\text{Ph}_2\text{P})_2\text{py}$ under reflux for 8 h produces a deep green solution from which green crystals of $\text{Rh}_4[\mu-(\text{Ph}_2\text{P})_2\text{py}]_2(\mu-\text{CO})(\text{CO})_2(\mu-\text{Cl})_2\text{Cl}_2$ (**3**) are isolated in 75% yield by the addition of ethyl



ether. The infrared spectrum shows the presence of both bridging and terminal carbonyl groups ($\nu(\text{CO})$ 1994, 1818, 1804 cm^{-1}) in dichloromethane solution, while the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum indicates that two equally populated, rhodium-bound phosphorus environments are present (δ_1 , 39.9, $^1J(\text{Rh},\text{P}) = 129.7$ Hz; δ_2 36.2 ppm, $^1J(\text{Rh},\text{P}) = 149.7$ Hz). The structure of the molecule, as determined by an X-ray crystal structure, is shown in Figure 2.⁶

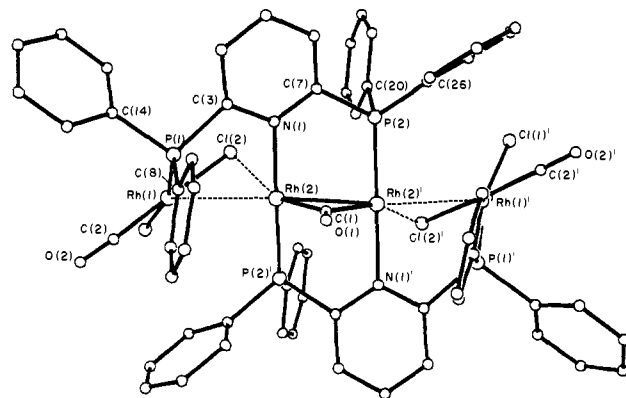
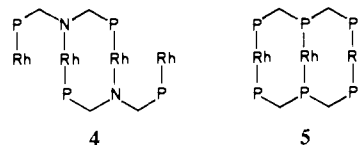
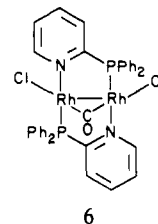


Figure 2. A perspective drawing of the structure of $[\mu-(\text{Ph}_2\text{P})_2\text{py}]_2\text{Rh}_4(\mu-\text{CO})(\text{CO})_2(\mu-\text{Cl})_2\text{Cl}_2$. Some significant interatomic distances and angles: Rh(1)–Rh(2), 2.921 (2); Rh(2)–Rh(2)', 2.594 (2); Rh(1)–Cl(1), 2.390 (6); Rh(1)–Cl(2), 2.355 (4); Rh(2)–Cl(2), 2.555 (5); Rh(1)–Cl(2), 1.88 (2); Rh(2)–Cl(1), 1.97 (2) Å; Rh(2)–Cl(1)–Rh(2), 82.5 (10)°; Rh(1)–Rh(2)–Rh(2)', 168.0(1)°; Rh(1)–Cl(2)–Rh(2), 73.0(2)°.

The molecule sits on a 2-fold rotation axis that passes through the bridging carbonyl and bisects the Rh(2)–Rh(2)' bond. Each phosphine ligand bridges three rhodium atoms. While these bridging ligands are trans to one another, their alignment involves a one-unit translation, **4**, which contrasts to the arrangement of



triphosphine ligands in $\text{Rh}_3(\mu\text{-dpmp})_3(\mu\text{-Cl})\text{Cl}(\text{CO})_3^+$, where the phosphines are exactly aligned, **5**.¹ The central portion of the structure of $[\mu-(\text{Ph}_2\text{P})_2\text{py}]_2\text{Rh}_4(\mu-\text{CO})(\text{CO})_2(\mu-\text{Cl})_2\text{Cl}_2$ is closely related to that of $\text{Rh}_2(\mu\text{-Ph}_2\text{Ppy})_2(\mu-\text{CO})\text{Cl}_2$ (**6**).⁷ Thus, the Rh(2)–Rh(2)' distance in **3**, 2.594 (2) Å, and the Rh–Rh distance in **6**, 2.612 (1) Å, are similar and indicative of the presence of



a metal–metal bond. In going from **6** to **3**, however, the terminal chloride ligands are absent, and in their place are the two Rh(2) atoms, each with a planar array of ligating atoms (2Cl, C, P). The Rh(1)–Rh(2) separation is significantly longer than the Rh(2)–Rh(2)' distance, but is shorter than the nonbonded Rh–Rh separations found in $\text{Rh}_3(\mu\text{-dpmp})_2(\mu\text{-Cl})\text{Cl}(\text{CO})_3^+$.¹ The position of Cl(2) indicates that it is semibridging with Rh(1)–Cl(2) and Rh(2)–Cl(2) distances of 2.354 (5) and 2.553 (5) Å, respectively. The latter distance is considerably longer than normal Rh–Cl bond lengths. The only other distance of similar length is found in $\text{Rh}_2(\mu\text{-dpm})_2(\mu-\text{CO})(\mu-\text{Cl})(\text{CO})_2^+$.⁸ The available evidence indicates that **3** retains its structure in solution.

Acknowledgment. We thank the National Science Foundation (CHE 7924575) for support. Acquisitions of the X-ray diffrac-

(4) For examples of chelating forms of Ph_2Ppy , see ref 3c and: Olmstead, M. M.; Maisonnat, A.; Farr, J. P.; Balch, A. L. *Inorg. Chem.* **1981**, *20*, 4060–4064.

(5) Yellow crystals of $[\mu-(\text{Ph}_2\text{P})_2\text{py}]_3\text{Pd}_3\text{Cl}_6 \cdot n\text{CH}_2\text{Cl}_2$ were grown by diffusion of ethyl ether into a dichloromethane solution of the complex. They belong to space group $P2_1/n$ with $a = 19.397$ (15), $b = 14.925$ (3), $c = 35.326$ (18) Å, $\beta = 98.6$ (5)°, $Z = 4$, $R = 0.12$ for 8520 reflections with $F > 3\sigma F$. The presence of several severely disordered molecules of dichloromethane have hampered our efforts to obtain a better R value.

(6) Green crystals of $[\mu-(\text{Ph}_2\text{P})_2\text{py}]_2\text{Rh}_4(\mu-\text{CO})(\text{CO})_2(\mu-\text{Cl})_2\text{Cl}_2 \cdot 2\text{CH}_2\text{Cl}_2 \cdot 2\text{N}_2$ were grown by diffusion of ethyl ether into a dinitrogen-saturated dichloromethane solution of the complex. They belong to the space group $I4_1$ (No. 80) with $a = 25.160$ (6), $c = 10.775$ (3) Å, $Z = 4$, $R = 0.048$ for 2258 reflections with $I > 2\sigma(I)$.

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tometer and NMR spectrometer used in these studies were made possible through NSF equipment grants. Fred E. Wood was a University of California Regents Fellow.

Supplementary Material Available: A list of atomic coordinates and thermal parameters for $[\mu-(\text{Ph}_2\text{P})_2\text{py}]_3\text{Pd}_3\text{Cl}_6$ and for $[\mu-(\text{Ph}_2\text{P})_2\text{py}]_2\text{Rh}_4(\mu-\text{CO})(\text{CO})_2(\mu-\text{Cl})_2\text{Cl}_2$ (3 pages). Ordering information is given on any current masthead page.

A Bis(dinitrogen) Complex of Molybdenum: A Chemical Resemblance to Nitrogenase?¹

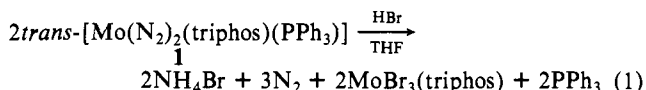
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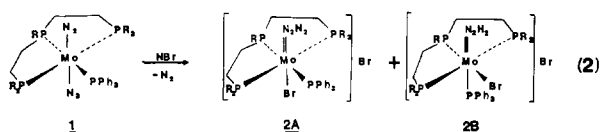
In 1978, Thorneley, Eady, and Lowe² reported the detection of hydrazine upon quenching the functioning enzyme nitrogenase with acid or base. On the basis of the chemistry of molybdenum and tungsten dinitrogen complexes they concluded that hydrazine was produced from an enzyme-bound dinitrogen hydride intermediate species upon quenching, and that neither hydrazine nor enzyme-bound hydrazine was an intermediate on the reduction route from dinitrogen (N_2) to ammonia.

We wish to report the first example of an analogous result in a noncatalytic ammonia-forming reaction (eq 1)³ in which hy-



drazine is not a product in the reaction but is detected upon early quenching of the reaction with water. Thus, reactions of *trans*- $\text{Mo}(\text{N}_2)_2(\text{triphos})(\text{PPh}_3)$ (**1**), where triphos = $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$, with anhydrous HBr in anhydrous tetrahydrofuran (THF) carried out over a period of ≥ 60 h produced high yields of ammonia (eq 1) but no more than traces of hydrazine (<0.0015 mol of N_2H_4 per mol of **1**).¹ However, when volatiles were removed in vacuo from reactions that had proceeded for only short periods of time (e.g., 1 h, see Figure 1) and a $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$ solvent mixture was added, hydrazine yields of up to 0.16 mol per mol of **1** were recorded.⁴ No free hydrazine was present before the addition of $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$ (see below).

Typically, reactions were carried out in one of two ways by using ca. 0.15 g (ca. 0.2 mmol) of **1** and ca. 20 mol of anhydrous HBr per mol of **1**. One method involved condensing HBr and THF onto **1** at -196°C and allowing the mixture to reach ambient temperature. After the mixture was stirred for a fixed period of time, all volatiles were removed in vacuo and CH_2Cl_2 (10 mL) and H_2O (25 mL) added. The aqueous layer was analyzed for ammonia and hydrazine.⁴ The second method involved the reaction of liquid HBr with **1** in the absence of solvent. Following the loss of 1.0 mol of N_2 per mol of **1**, a green-brown solid mixture of two isomeric hydrazido(2-) complexes resulted (eq 2).^{1,5} It



(1) Reactions of Coordinated Dinitrogen. 13. Part 12: Bossard, G. E.; George, T. A.; Howell, D. B.; Koczon, L. M.; Lester, R. L. *Inorg. Chem.* **1983**, *22*, 1968-1970.

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(3) Baumann, J. A.; George, T. A. *J. Am. Chem. Soc.* **1980**, *102*, 6153-6154.

(4) See ref 3 for details of ammonia and hydrazine analyses.

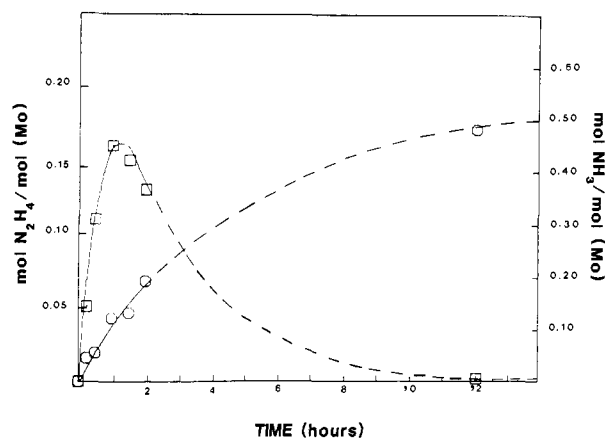
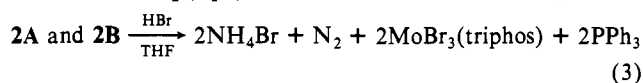


Figure 1. Variations in yields of hydrazine and ammonia vs. time. In separate experiments the reaction of **1** with HBr in THF was stopped after 0.25, 0.5, 1.0, 1.5, 2.0, and 12 h. At 60 h or longer, the yields of ammonia and hydrazine are routinely 0.72 and <0.0015 mol per mol of **1**.

is these two hydrazido(2-) complexes that react further to afford ammonia and N_2 (eq 3). To this solid was added THF, and the



reaction was allowed to proceed for a fixed period of time. An identical workup procedure with that described above was used. Both methods gave similar results.

The yields of ammonia and hydrazine were plotted as a function of time (see Figure 1). Early in the reaction, following the loss of 1.0 mol of N_2 , a rapid buildup of hydrazine was observed while the amount of ammonia produced was small. As the reaction proceeded a maximum yield of hydrazine was observed after 1.0 h beyond which time the yield continued to decrease. The ammonia yield (and further N_2 evolution) increased steadily with time.

The relatively rapid buildup of hydrazine corresponds very closely with the decrease in intensities of resonances due to **2B** (totally absent within 1 h) and the appearance of PPh_3 in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a mixture of HBr, **2A**, and **2B** in THF.¹ No new species, other than PPh_3 , were seen in the spectrum. Hydrazine could be being formed at this stage in the reaction and behaving as an intermediate on the route to ammonia. In order to investigate this possibility solid **1** was treated with liquid HBr to produce a mixture of **2A** and **2B**. Upon cooling to -196°C , evolved N_2 was removed in vacuo, and $^{15}\text{N}_2\text{H}_4$ ⁶ and THF were added. The reaction mixture was allowed to stir for 60 h at which time the evolved gases were collected. The aqueous extract was treated with a NaOBr solution and the gases were collected. Mass spectral determination of the ratio of N_2 isotopomers provided no evidence that $^{15}\text{NH}_4^+$ (as determined from N_2 -29) had been produced in yields any greater than the background. In other words, there is no evidence for incorporation of $^{15}\text{N}_2\text{H}_4$ (present as $^{15}\text{N}_2\text{H}_5\text{Br}$) into the ammonia-forming sequence of reactions.⁷

These results suggest that early in the reaction a metal-bound dinitrogen hydride intermediate species is present in high concentration that leads to ammonia under normal reaction conditions. However, upon treatment with water this intermediate⁸ produces hydrazine. That dioxygen plays no part in hydrazine formation was demonstrated by using scrupulously outgassed water and showing no decrease in the yield of hydrazine after 1 h.

(5) The ratio of **2A** to **2B** is ca. 1:2.

(6) Prepared from $^{15}\text{N}_2\text{H}_6\text{SO}_4$: Browne, A. W.; Welsh, T. W. B. *J. Am. Chem. Soc.* **1911**, *33*, 1728-1734.

(7) The transitory existence of hydrazine within a solvent cage or bound to a metal cannot be eliminated by this experiment. However, the large yields of hydrazine determined early in the reaction after workup argue against these likelihoods.

(8) We believe that hydrazine is produced from the same intermediate in the reactions of **1** with HBr in benzene and toluene.¹