

to the diethylamino derivative upon reaction with diethylamine.

In the reactions of the chlorophosphole with  $\text{AgNCO}$ ,  $\text{AgNCS}$ ,  $\text{C}_6\text{H}_5\text{SH}$ ,  $\text{CH}_3\text{SH}$ , and  $\text{CH}_3\text{OH}$ ,<sup>4</sup> spectroscopic data indicated that the isolated products were, respectively, I, where  $\text{X} = \text{NCO}$ ,  $\text{NCS}$ ,  $\text{SC}_6\text{H}_5$ ,  $\text{SCH}_3$ , and  $\text{OCH}_3$ . However, these phospholes changed their identity rapidly, and we were unable to obtain pure samples for satisfactory identification and further reaction with  $\text{W}(\text{CO})_5 \cdot \text{THF}$ . The literature contains many examples of the lability of phospholes toward Arbuzov and similar reactions.<sup>5</sup> Attempts to stabilize the labile ligands, by immediate reaction with the tetrahydrofuran complex of tungsten pentacarbonyl, in many cases gave isolatable complexes which decomposed rapidly both *in vacuo* and under nitrogen to give uncharacterized blue residues. In contrast, the new compounds  $\text{C}_6\text{H}_4\text{O}_2\text{P}(\text{Cl})\text{W}(\text{CO})_5$  and  $\text{C}_6\text{H}_4\text{O}_2\text{P}[\text{N}(\text{C}_2\text{H}_5)_2]\text{W}(\text{CO})_5$  have been stable for up to 2 years in a nitrogen atmosphere.

The reactions of the chlorophosphole with silver cyanide (in dichloromethane and in xylene, under reflux) and with methyl- or phenylmagnesium bromide did not yield the desired derivatives of I. Furthermore, we were unable to obtain a pure sample of the phenylphosphole from the reaction of phenylphosphorus dichloride with catechol.<sup>6,7</sup>

The proton nmr spectrum of the aminophosphole-tungsten pentacarbonyl complex, when compared to that for the uncomplexed ligand, shows a downfield shift for all the ligand protons consistent with a formal oxidation state change from 3+ to 5+ for phosphorus upon complexation (assuming that phosphorus is coordinating to tungsten).

#### Experimental Section

**Physical Measurements.**—Infrared spectra were determined using a Perkin-Elmer Model 21 sodium chloride spectrophotometer and a Perkin-Elmer 621 grating spectrometer. Proton nmr spectra were obtained by means of a Varian A-60 spectrometer using tetramethylsilane as an internal standard. Mass spectra were taken using a Perkin-Elmer Hitachi RMU-6D double-focusing spectrometer at 70-eV ionizing energy. Irradiation was carried out in a quartz vessel using a Hanovia 679A36 medium-pressure lamp. Analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., and Micro-Tech Laboratories, Inc., Skokie, Ill.

**Materials.**—Tungsten hexacarbonyl was a generous gift from the Climax Molybdenum Co. 2-Chloro-1,3,2-benzodioxaphosphole was prepared by a literature method<sup>4</sup> and all solvents were dried before use by standard procedures. All manipulations were carried out under nitrogen.

**Preparation of  $\text{C}_6\text{H}_4\text{O}_2\text{P}(\text{Cl})\text{W}(\text{CO})_5$  (II).**—A solution of 1.76 g (5 mmol) of tungsten hexacarbonyl in 50 ml of tetrahydrofuran was irradiated for 5 hr, during which time 5 mmol of carbon monoxide was evolved. The resulting yellow solution was added quickly to 0.87 g (5 mmol) of  $\text{C}_6\text{H}_4\text{O}_2\text{PCl}$  and the mixture was stirred for 20 min at ambient temperature. Solvent was removed *in vacuo* and the residual yellow solid sublimed. Unreacted tungsten hexacarbonyl (0.35 g) was collected at 30° (0.05 mm) and identified by its infrared spectrum. Fine colorless needles of product (0.75 g, 40%) were collected at 50–55° (0.05 mm), mp 80–81°. *Anal.* Calcd for  $\text{C}_{11}\text{H}_4\text{ClO}_7\text{PW}$ : C, 26.5; H, 0.8; Cl, 7.1. Found: C, 26.5; H, 1.1; Cl, 7.2. Ir spectrum (hexane solution):  $\nu(\text{CO})$  2083 (m), 1981 (vs), 1950 (m sh)  $\text{cm}^{-1}$ . A parent ion was observed in the mass spectrum at 500 (calcd: 500 for  $^{184}\text{W}$  and  $^{37}\text{Cl}$ ).

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**Preparation of 2-Diethylamino-1,3,2-benzodioxaphosphole,  $\text{C}_6\text{H}_4\text{O}_2\text{PN}(\text{C}_2\text{H}_5)_2$ .**—A 2.9-g (40-mmol) sample of diethylamine in 20 ml of benzene was added dropwise, over a 4-hr period, to 3.5 g (20 mmol) of 2-chloro-1,3,2-benzodioxaphosphole in 20 ml of benzene, cooled to 0° in a two-necked flask equipped with a mechanical stirrer. Vigorous stirring was maintained for a further 16 hr at ambient temperature under nitrogen. Solvent was removed *in vacuo* and the residue was shaken with pentane. The mixture was filtered, solvent was removed, and the residual oil was distilled under reduced pressure. The product (1.9 g, 46%) was collected at 113–115° (0.25 mm). *Anal.* Calcd for  $\text{C}_{10}\text{H}_{14}\text{NO}_2\text{P}$ : C, 56.9; H, 6.6; N, 6.6; P, 14.7. Found: C, 58.4; H, 6.9; N, 6.4; P, 14.0. Proton nmr (carbon tetrachloride solution):  $\tau$  3.23 (four phenyl protons), 7.14 (six methylene protons), 9.02 (six methyl protons).

**Preparation of  $\text{C}_6\text{H}_4\text{O}_2\text{P}[\text{N}(\text{C}_2\text{H}_5)_2]\text{W}(\text{CO})_5$ .**—The preparation was essentially the same as for II above [0.88 g (2.5 mmol) of tungsten hexacarbonyl, 7 hr irradiation, and 0.52 g (2.5 mmol) of ligand]. After removal of solvent the pink solid was sublimed to give 0.13 g of unreacted tungsten hexacarbonyl (40° (0.05 mm)) and fine colorless needles of product (0.76 g, 67%) at 75° (0.05 mm), mp 67°. *Anal.* Calcd for  $\text{C}_{18}\text{H}_{14}\text{NO}_7\text{PW}$ : C, 33.7; H, 2.6; P, 5.8; W, 34.4. Found: C, 33.9; H, 2.6; P, 5.9; W, 33.3 Ir spectrum (hexane solution):  $\nu(\text{CO})$  2081 (m), 1962 (vs)  $\text{cm}^{-1}$ . A parent ion was observed in the mass spectrum at 535 (calcd: 535 for  $^{184}\text{W}$ ). Proton nmr (carbon tetrachloride solution):  $\tau$  3.07 (four phenyl protons), 6.82 (four methylene protons), 8.84 (six methyl protons).

**Reaction of 2-Chloro-1,3,2-benzodioxaphosphole with Silver Isothiocyanate.**—A 8.73-g (50-mmol) sample of 2-chloro-1,3,2-benzodioxaphosphole and 8.30 g (50 mmol) of silver isothiocyanate in 100 ml of benzene were heated under reflux for 16 hr. The cooled mixture was filtered, solvent was removed *in vacuo*, and the residual viscous liquid was distilled. The main fraction (5.15 g) was collected at 70° (1.5 mm). The mass spectrum showed a parent ion at 197 which agrees with the calculated value of 197 for  $\text{C}_7\text{H}_4\text{NO}_2\text{PS}$ . However, this product rapidly turned into a yellow-orange oil upon standing at room temperature, *in vacuo*, in the dark.

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## The Nitrogen 1s Binding Energies of Transition Metal Nitrosyls

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The bonding and electronic structure of transition metal nitrosyls have been frequently studied in recent years.<sup>1–6</sup> Two limiting situations have been identified: linearly coordinated  $\text{NO}^+$  groups and angularly coordinated ("bent")  $\text{NO}^-$  groups. We have investigated the X-ray photoelectron spectra<sup>7</sup> of a series of these compounds to attempt correlations of the nitro-

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gen 1s electron binding energy with structure,<sup>8-19</sup> electronic features, and N-O stretching frequency.<sup>16,20-39</sup>

### Experimental Section

The compounds were kindly supplied by Philip G. Douglas and Robert D. Feltham of the University of Arizona, by G. Dolcetti, P. Farnham, and James P. Collman of Stanford University, and, in the case of  $[\text{Co}(\text{NH}_3)_5\text{NO}]\text{Cl}_2$ ,<sup>40</sup> by Mark Iannone of this department.

The powdered samples were brushed onto double-faced conducting tape attached to an aluminum plate. The reproducibility was  $\pm 0.2$  eV. In each case the carbon 1s line (due to a film of pump oil on the samples) was recorded and used as a reference peak. Individual lines had widths at half-height of 1.2-2.8 eV; broader lines were due to decomposition or to the presence of a second peak.

The kinetic energy of the photoelectron,  $E_K$ , was measured in an iron-free double-focusing magnetic spectrometer<sup>41</sup> in which the incident radiation,  $E_{h\nu}$ , was magnesium  $K\alpha$  X-radiation (1253.6 eV) and for which the work function,  $\phi_s$ , was taken as 4.0 eV. The nitrogen 1s binding energy,  $E_B$  (the difference between the Fermi level and the 1s atomic level energy), was calculated from the relation  $E_B = E_{h\nu} - E_K - \phi_s$ .

### Results and Discussion

The data are presented in Table I. It was found advantageous to categorize the compounds in terms of the metal d-electron configurations by making the arbitrary assumption that the nitrosyl groups were  $\text{NO}^+$  ions. (Although this assumption is illogical for the few compounds that contain "bent" NO groups, we made the assumption to simplify the classification of the compounds.)

The first seven compounds in Table I are six-co-

ordinate and formally have five or six d-electrons. In compounds 1-4, the metal atoms are in "abnormally low" oxidation states (0, 1+, and 1+ for Mo, Cr, and Mn, respectively), whereas in 5-7, the metal atoms are in "normal" oxidation states (2+ for Ru and Fe). As far as is known, the NO groups in these seven compounds are essentially linearly coordinated. The nitrogen 1s binding energies are all within  $\pm 0.6$  eV of 400.1 eV except for 6 and 7, for which the binding energies are 402.9<sup>42</sup> and 403.3 eV, respectively. The high values for the latter compounds are indicative of relatively high positive charges on the NO groups and may be rationalized by the fact that in these compounds the metal atoms are in a "normal" oxidation state. It is noteworthy that the N-O stretching frequencies for 6 and 7 are very high—a further indication of minimal electron donation into the  $\pi$  orbitals of the  $\text{NO}^+$  groups. It is difficult to explain the low binding energy observed for 5, which contains ruthenium in a "normal" oxidation state and which has a very high N-O stretching frequency. Perhaps the recorded binding energy corresponds to a decomposition product.<sup>42</sup>

The second set of compounds in Table I formally have seven or eight d electrons and are either five- or six-coordinate.<sup>43</sup> Most of the binding energies lie within  $\pm 0.4$  eV of 400.3 eV; the two exceptions are 10 and 15, with binding energies of 401.5 and 402.3 eV, respectively. It may be significant that both of the latter compounds are five-coordinate; one would expect a lower electron density on the metal and the attached nitrosyl group in a five-coordinate complex than in a six-coordinate complex. However, the low binding energies of the other two five-coordinate complexes, 9 and 11, are then difficult to rationalize. In this set of eight compounds, 15 has both the highest binding energy and the highest N-O stretching frequency.

It is interesting that, although 8 contains both terminal and bridging NO groups,<sup>28</sup> only one nitrogen 1s peak was observed. Apparently, the NO groups are so similar in electron density that they are indistinguishable by X-ray photoelectron spectroscopy.

A binding energy of 402.0 eV was previously reported<sup>44</sup> for 13,  $[\text{Co}(\text{NO})(\text{NH}_3)_5]\text{Cl}_2$ . We repeated this measurement several times with samples that were shown to be pure by magnetic susceptibility measurements and consistently observed one slightly broadened peak due to the  $\text{NH}_3$  groups (at 400.2 eV) and the NO group. By computer fitting, we were unable to ascertain the position of the NO peak more precisely than  $400.7 \pm 1.3$  eV.

It should be noted that, on going from 14 to 15, the complex ion changes only by the removal of a chloride ion—with the consequent change in coordination number from 6 to 5. The increase in binding energy of 1.8 eV and the increase in the N-O stretching frequency of  $300 \text{ cm}^{-1}$  are the expected consequences of reduced electron donation into the  $\text{NO}^+$   $\pi$  orbitals.

(42) Compound 6 underwent decomposition in the X-ray beam, as evidenced by a gradual decrease in the 402.9-eV peak and the simultaneous growth of a 400.0-eV peak. Although no similar evidence for decomposition was noticed in the case of compound 5, it is possible that such decomposition occurred before adequate counts for a decent spectrum were obtained.

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TABLE I  
NITROGEN 1s BINDING ENERGIES, N-O STRETCHING FREQUENCIES, AND M-N-O BOND ANGLES FOR SOME  
TRANSITION METAL COMPLEXES

Compd no.	Compd	No. of d electrons <sup>a</sup>	Nitrogen 1s binding energy, eV	Nitrosyl str freq, cm <sup>-1</sup>	Ref	M-N-O angle, deg	Ref
1	MoCl <sub>2</sub> (NO) <sub>2</sub> (diars)	6	399.6	1760, 1670	20		
2	<i>trans</i> -[CrCl(NO)(diars) <sub>2</sub> ]ClO <sub>4</sub>	5	400.7	1690	20		
3	K <sub>3</sub> [Cr(NO)(CN) <sub>5</sub> ]	5	400.7 <sup>b</sup>	1645	21	176.0 <sup>c</sup>	8
4	[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P] <sub>3</sub> [Mn(NO)(CN) <sub>5</sub> ]·3H <sub>2</sub> O	6	399.7	1725 <sup>d</sup>	22	174.3 <sup>d</sup>	9
5	<i>trans</i> -[RuCl(NO)(diars) <sub>2</sub> ]Cl <sub>2</sub>	6	400.0	1883	23		
6	<i>trans</i> -[FeCl(NO)(diars) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	6	402.9 <sup>e</sup>	1865	24		
7	Na <sub>2</sub> [Fe(NO)(CN) <sub>5</sub> ]·2H <sub>2</sub> O	6	403.3	1939	25	178.3	10
8	[π-C <sub>6</sub> H <sub>5</sub> Cr(NO) <sub>2</sub> ] <sub>2</sub>	7	400.7	1672, 1505	26		
9	RhI <sub>2</sub> (NO)[P(CH <sub>3</sub> )(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ] <sub>2</sub>	8	400.3	1628 <sup>f</sup>	27	120 <sup>g</sup>	11
10	RhCl <sub>2</sub> (NO)[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub>	8	401.5	1630	28	123 <sup>h</sup>	12
11	CoCl <sub>2</sub> (NO)(diphos)	8	400.7	1676	29		
12	<i>trans</i> -[FeCl(NO)(diars) <sub>2</sub> ]ClO <sub>4</sub>	7	400.0	1620	30		
13	[Co(NO)(NH <sub>3</sub> ) <sub>5</sub> ]Cl <sub>2</sub>	8	400.7	1620	31	119.0	13
14	<i>trans</i> -[CoCl(NO)(diars) <sub>2</sub> ]Cl	8	400.5	1562, 1548	32	124.4 <sup>i</sup>	14
15	[Co(NO)(diars) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	8	402.3	1852	32	174 <sup>j</sup>	15
16	CoCl <sub>2</sub> (NO)[P(CH <sub>3</sub> )(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ] <sub>2</sub>	8	401.7, 399.6	1735, 1630	28		
17	CoCl <sub>2</sub> (NO)[P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> ] <sub>2</sub>	8	401.5, 399.7	1720, 1650	28		
18	[Fe(NO)(diars) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	7	401.2, 399.6	1760	30		
19	{RuCl(NO) <sub>2</sub> [P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> }PF <sub>6</sub>	8	402.6, 400.2	1845, 1687	16	179.5, 136.0	16
20	{Rh(NO) <sub>2</sub> [P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> }PF <sub>6</sub>	10	401.1	1730, 1720	33		
21	{Ir(NO) <sub>2</sub> [P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> }PF <sub>6</sub>	10	400.2	1760-1715	34	163.5	17
22	Co(NO)[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>3</sub>	10	400.0	1738	35		
23	Co(NO)(CO)[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub>	10	400.8	1714	35		
24	Rh(NO)[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>3</sub>	10	400.8	1650	36		
25	Ir(NO)[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub>	10	400.3	1615	37	180	18
26	Ir(NO)(CO)[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub>	10	399.6	1645	37		
27	Ru <sub>3</sub> (NO) <sub>2</sub> (CO) <sub>10</sub>	10	400.4 <sup>k</sup>	1524, 1508	38		
28	NiCl(NO)[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub>	10	399.8	1735 <sup>l</sup>	39		
29	Ni(N <sub>3</sub> )(NO)[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub>	10	399.6			152.7	19

<sup>a</sup> Based on the arbitrary assumption of NO<sup>+</sup> nitrosyl groups. <sup>b</sup> D. Hendrickson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, **8**, 2642 (1969). <sup>c</sup> The bond angle refers to the corresponding Co(en)<sub>3</sub><sup>3+</sup> salt. <sup>d</sup> Both the stretching frequency and bond angle are for the corresponding potassium salt. <sup>e</sup> Reference 42. <sup>f</sup> The stretching frequency is for the compound containing the triphenylphosphine ligand. <sup>g</sup> The bond angle refers to the analogous iridium complex in which one CH<sub>3</sub> group has been replaced by an I atom. <sup>h</sup> The bond angle refers to the analogous iridium complex. <sup>i</sup> The bond angle refers to the analogous compound in which ethylenediamine groups have replaced the diarsine groups. <sup>j</sup> The bond angle refers to the analogous ruthenium complex in which two diphosphine groups have replaced the diarsine groups. <sup>k</sup> Very broad signal because of decomposition. <sup>l</sup> The stretching frequency is for the analogous bromo and iodo compounds.

The third set of compounds in Table I formally have seven or eight d electrons and show two separate nitrogen 1s peaks. For each of the cobalt compounds 16 and 17, two different coordination geometries are thought to be present:<sup>28</sup> a trigonal-bipyramidal structure with an equatorial linear nitrosyl and a square-pyramidal structure with an apical bent nitrosyl. The two nitrogen 1s binding energies observed for both of these compounds are separated by about 2 eV. Presumably the bent nitrosyl corresponds to the lower binding energy and the linear nitrosyl corresponds to the higher binding energy in each case.

Two nitrogen 1s binding energies were observed for 18, [Fe(NO)(diars)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, although only one N-O stretching frequency has been reported. Three possible explanations come to mind. Perhaps different structural forms are present (as postulated for 16 and 17), and the N-O stretching frequency of one form is of low intensity. Perhaps the spectral splitting is due to the paramagnetism of the sample. Finally, it is not unlikely that the sample underwent decomposition in the X-ray beam and that the two peaks are due to the compound and its decomposition product.<sup>45</sup>

In the ruthenium complex, compound 19, two different types of nitrosyl group are bonded to the same metal atom.<sup>16</sup> This square-pyramidal compound has

(45) However, we were unable to observe any evidence of a shift in the relative intensities of the peaks with time of irradiation.

an apical bent nitrosyl and a linear equatorial nitrosyl. Presumably, the higher binding energy (402.6 eV) and higher N-O frequency (1845 cm<sup>-1</sup>) correspond to the linear nitrosyl, and the lower binding energy (400.2 eV) and lower N-O frequency (1687 cm<sup>-1</sup>) correspond to the bent nitrosyl.

The fourth set of compounds in Table I (20-29) formally have ten d electrons and, except for 27, are four-coordinate. Probably because of the high electron densities on the metal atoms, the binding energies are low. The low N-O stretching frequencies are consistent with these results.

We draw the overall conclusion that there is a definite correlation between the nitrogen 1s binding energy of a nitrosyl group and the electron density on that group. Bent nitrosyls have low binding energies. Linear nitrosyls can have either low or high binding energies, depending on the extent of π back-bonding from the metal atom. The binding energies are at least roughly correlated with the N-O stretching frequencies: when one is high or low, so is the other.

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