

thogonal. In the second case (II), complete delocalization over the two sites is assumed. In the former, noninteracting case, the E° values for the oxidations of A to A^+ and A' to $(A')^+$ differ by only a small statistical factor (35.6 mV at 298 K), and in CV studies one reversible-looking wave (of two-electron height) is observed.^{8m,46} In the latter extreme of strongly interacting A and A' sites, E° separations of ca. 0.5 V are observed.⁴⁷

For linked ferrocene systems, the ΔE° arguments are supported by spectroscopic conclusions in the extremes of large and small ΔE° values. For example, bis(fulvalene)diiron, **13**, which is highly delocalized, has $\Delta E^\circ = 580 \text{ mV}^{8c}$ for the processes $13/13^+$ and $13^+/13^{2+}$, while 1,2-diferrocenylethane, which forms a metal-localized monocation, has $\Delta E^\circ = \text{ca. } 40 \text{ mV}^{8c}$. Our present dichromium complexes follow this trend, with $\Delta E^\circ \geq 500 \text{ mV}$ for the two oxidations of delocalized **8-10**, but only $\Delta E^\circ = 120 \text{ mV}$ for $11/11^+/11^{2+}$.

However, intermediate values of ΔE° or relatively small changes in ΔE° should be viewed with caution in trying to make conclusions about minor changes in delocalization. The actual ΔE° is affected not only by charge delocalization but also by differences in the change of solvation or ion pairing in the two redox steps and structural changes during or following the electron transfers.^{6a,8m,48} These factors have been adequately identified, but not quantified, for binuclear complexes, and further investigations are warranted.

Conclusions

These studies show that a new class of formally mixed-valent homodinuclear cations has been prepared, based on the linkage

(45) Moore, M. F.; Wilson, S. R.; Hendrickson, D. N.; Mueller-Westerhoff, U. T. *Inorg. Chem.* **1984**, *23*, 2918.

(46) Ammar, F.; Saveant, J. M. *J. Electroanal. Chem.* **1973**, *47*, 215.

(47) Phelps, J.; Bard, A. J. *J. Electroanal. Chem.* **1976**, *68*, 313.

(48) (a) Goldsby, K. A.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 3002. (b) Richardson, D. E.; Taube, H. *J. Am. Chem. Soc.* **1983**, *105*, 40.

(49) Geiger et al. *J. Electroanal. Chem.* **1987**, *222*, 151.

of (arene)chromium dicarbonyl phosphine units. The monocation **7⁺** linked only through the biphenyl ligand is a completely localized mixed-valent complex on the vibrational and ESR time scales, with one Cr(I) and one Cr(0) site. The doubly-linked complex **8** displays a severe twist of the biphenyl ligand around the interconnecting C-C bond. The twist relaxes in the monocation of **8**, with the biphenyl moiety having nearly coplanar aryl rings. This structure allows complete delocalization of the charge over the two halves of the molecule. The doubly linked complexes **8** and **8⁺** thus join a slowly growing but important list of binuclear mixed-valent organometallics that have been structurally characterized in two oxidation states.^{8q,r,u,10,11,45} Certainly this structural information will be important in further deciphering the mechanism of intramolecular charge transfer in mixed-valent complexes.

The separations of standard potentials of the two successive one-electron oxidations of these compounds follow the previously observed trend that totally delocalized systems have considerably larger ΔE° values than those not exhibiting electronic delocalization. However, the quantitative relationship between ΔE° and electronic delocalization is unclear. Since structural changes are expected to play a role in ΔE° values, they may contribute significantly to the values for **8** and its analogues, increasing ΔE° because of the thermodynamic stabilization of **8⁺** by rotation of the aryl rings toward coplanarity.

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Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom coordinates, bond distances, and bond angles for **8** and **8⁺** (13 pages); listings of observed and calculated structure factors for **8** and **8⁺** (43 pages). Ordering information is given on any current masthead page.

Synthesis and Structure of 2,4-Bis(2,6-di-*tert*-butyl-4-methylphenoxy)- 1,3,2,4-dioxadiphosphetane. An Aryl Phosphenite Dimer

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Abstract: When 2,4,6-tris(2,6-di-*tert*-butyl-4-methylphenoxy)-1,3,5,2,4,6-trioxatriphosphorinane (**1a**) is sublimed at 220 °C under vacuum, a new heterocycle, a 1,3,2,4-dioxadiphosphetane (**3**), is formed. This molecule can be considered a dimer of the aryl phosphenite **2**. Molecule **3** crystallizes in the $P2_1/c$ space group of the monoclinic crystal system with four molecules per unit cell. The X-ray crystal structure of **3** reveals that the P_2O_2 heterocycle exists as a bent rhombus wherein the four ring atoms do not all lie in the same plane. The two 2,6-di-*tert*-butyl-4-methylphenoxy groups are in a *cis* configuration but the molecule does not possess a plane of symmetry. Using ^{31}P NMR to follow the synthesis of **1a**, we observed the formation and disappearance of **3**. While **3** is stable in THF/ $CDCl_3$ solution, it readily converts to **1a** upon addition of amine. These data suggest the intermediacy of **2**.

In a recent publication,¹ we discussed the syntheses, characterizations, and crystal structures of **1a** and **1b**, the first P(III) structures of their kind. These molecules were viewed as the cyclic

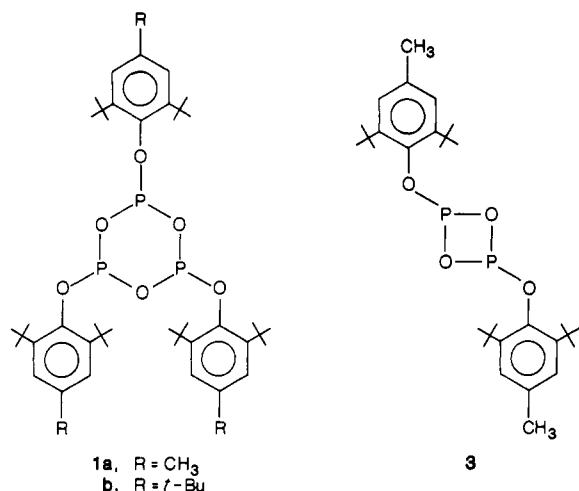
trimers of the corresponding monomeric aryl phosphenite **2**. However, while the stoichiometry of the reaction leading to **1** suggested the possible intermediacy of **2**, no other experimental data were available. As part of a continuing study to understand

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(1) Chasar, D. W.; Fackler, J. F., Jr.; Komoroski, R. A.; Kroenke, W. J.; Mazany, A. M. *J. Am. Chem. Soc.* **1986**, *108*, 5956-5962.



the mechanism of formation of **1**, we elected to examine the thermal chemistry associated with **1**. We now report the first synthesis and total structural characterization of a novel 1,3,2,4-dioxadiphosphetane **3**, a four-membered ring of trivalent phosphorus and oxygen.² **3** can be viewed as the cyclic dimer of the aryl phosphenite **2**.

Results and Discussion

Compound **3** was prepared by a vacuum sublimation of **1**³ (see Experimental Section). Table I summarizes the crystal data and final refinement of the structure. Tables II–IV summarize the atomic positions of all non-hydrogen atoms, and the bond angles that involve the P and O atoms. The ORTEP drawing of the molecular structure of **3** showing the 50% probability thermal ellipsoids is shown as Figure 1. The central feature of the structure is a four-membered ring of alternating P and O atoms approximately in the shape of a rhombus. However, the P₂O₂ atoms do not lie in the same plane. This slight deviation from planarity is illustrated in Figure 2, which also emphasizes the *cis* arrangement of the 2,6-di-*tert*-butyl-4-methylphenoxy groups that are bound to the P₂O₂ rhombus. This *cis* arrangement was unexpected. We anticipated a *trans* arrangement in order to minimize intramolecular interactions between the bulky phenoxy groups. We predict that if **3** could be isolated in the *trans* arrangement, the central P₂O₂ ring would be planar, and the molecule would possess a center of symmetry.

Although it appears from Figures 1 and 2 that this dioxadiphosphetane molecule might have *m* symmetry, the "right" half of **3** (defined by O₁, P₁, O₂, and the O₄ phenoxy group) is not crystallographically equivalent to the "left" half (defined by O₁, P₂, O₂, and the O₃ phenoxy group). That is, there is no mirror plane of symmetry passing through O₁ and O₂, and the molecule is asymmetric. Both the deviation of the P₂O₂ ring from planarity and the deviation from *m* symmetry appear to result from intramolecular steric interactions between the opposing phenoxy groups rather than from intermolecular interactions. The repulsive force between the two phenoxy groups bends the P₂–O₃ and P₁–O₄ bonds away from each other and forces P₁ and P₂ out of an ideal planar configuration with O₁ and O₂. As shown in Figure 2, the two halves of the molecule behave as if they are hinged together along an imaginary line drawn between O₁ and O₂.

Scheme 1 shows that **3** can be considered the cyclic dimer of the aryl phosphenite **2**. In the same way, the trioxatriphosphorinane **1**² can be considered the trimer of **2**. Therefore, it is instructive to compare the P–O distances and the P–O–P and O–P–O angles in the dimer and trimer molecules. In the dimer, the four P–O distances are equivalent within the P₂O₂ rhombus, averaging 1.666 ± 0.005 Å. The six P–O distances in the distorted

Table I. Crystal Data and Final Refinements for **3**

mol formula	C ₃₀ H ₄₆ O ₄ P ₂
color	colorless
cryst dims, mm	0.3 × 0.4 × 0.2
cryst class	monoclinic
space group	P2 ₁ /c
cell dims	
<i>a</i> , Å	14.938 (3)
<i>b</i> , Å	11.626 (3)
<i>c</i> , Å	18.376 (3)
β, deg	105.07 (1)
molecules/cell	4
cell vol, Å ³	3081.59
density, g/cm ³	1.15
wavelength, Å	0.71073
<i>M_r</i>	532.64
linear abs coeff, cm ⁻¹	1.76
reflns with <i>F</i> > 3σ(<i>F</i>)	2780
final residuals	
<i>R</i>	0.042
<i>R_w</i>	0.055

Table II. Atom Positions for **3**

atom	<i>X/a</i>	<i>Y/b</i>	<i>Z/c</i>
P(1)	0.1106 (1)	0.4653 (1)	0.1898 (1)
P(2)	0.1912 (1)	0.3503 (1)	0.3010 (1)
O(1)	0.1368 (1)	0.4761 (2)	0.2838 (1)
O(2)	0.1751 (2)	0.3467 (2)	0.2080 (1)
O(3)	0.2971 (1)	0.3931 (2)	0.3299 (1)
O(4)	0.1823 (1)	0.5533 (2)	0.1675 (1)
C(11)	0.1211 (2)	0.7415 (3)	0.1239 (2)
C(12)	0.0769 (2)	0.8093 (3)	0.0621 (2)
C(13)	0.0650 (2)	0.7756 (3)	-0.0113 (2)
C(14)	0.1040 (2)	0.6727 (3)	-0.0244 (2)
C(15)	0.1488 (2)	0.5982 (3)	0.0333 (2)
C(16)	0.1493 (2)	0.6325 (3)	0.1069 (2)
C(21)	0.3678 (2)	0.3778 (3)	0.4641 (2)
C(22)	0.4275 (2)	0.3150 (3)	0.5222 (2)
C(23)	0.4784 (2)	0.2231 (3)	0.5093 (2)
C(24)	0.4744 (2)	0.1942 (3)	0.4358 (2)
C(25)	0.4177 (2)	0.2506 (3)	0.3746 (2)
C(26)	0.3614 (2)	0.3378 (3)	0.3912 (2)
C(31)	0.1942 (2)	0.4880 (3)	0.0128 (2)
C(32)	0.2054 (3)	0.4925 (4)	-0.0678 (2)
C(33)	0.1341 (3)	0.3825 (4)	0.0150 (3)
C(34)	0.2911 (3)	0.4728 (5)	0.0652 (3)
C(41)	0.1373 (3)	0.7923 (3)	0.2042 (2)
C(42)	0.2361 (3)	0.7679 (4)	0.2505 (2)
C(43)	0.0666 (4)	0.7433 (4)	0.2429 (2)
C(44)	0.1248 (4)	0.9232 (4)	0.2012 (2)
C(51)	0.0108 (3)	0.8488 (3)	-0.0757 (2)
C(61)	0.3161 (3)	0.4831 (3)	0.4852 (2)
C(62)	0.2186 (3)	0.4466 (4)	0.4882 (3)
C(63)	0.3685 (3)	0.5316 (4)	0.5630 (2)
C(64)	0.3108 (3)	0.5839 (3)	0.4310 (2)
C(71)	0.4196 (3)	0.2154 (4)	0.2943 (2)
C(72)	0.4240 (4)	0.3215 (4)	0.2456 (2)
C(73)	0.3343 (4)	0.1396 (4)	0.2591 (3)
C(74)	0.5067 (3)	0.1449 (4)	0.2948 (2)
C(81)	0.5412 (3)	0.1576 (4)	0.5739 (2)

Table III. Selected Bond Distances (Å) for **3**

P(1)–O(1)	1.673 (2)	P(2)–O(3)	1.611 (2)
P(1)–O(2)	1.665 (3)	O(3)–C(26)	1.429 (4)
P(1)–O(4)	1.609 (2)	O(4)–C(16)	1.431 (4)
P(2)–O(1)	1.662 (3)	P(1)···P(2)	2.476 (1)
P(2)–O(2)	1.663 (2)	O(1)···O(2)	2.223 (3)

Table IV. Selected Bond Angles (Deg) for **3**

P(1)–O(1)–P(2)	95.88 (14)	O(1)–P(2)–O(3)	100.41 (12)
P(1)–O(2)–P(2)	96.16 (13)	O(2)–P(1)–O(4)	100.88 (12)
O(1)–P(1)–O(2)	83.48 (12)	O(2)–P(2)–O(3)	102.33 (12)
O(1)–P(2)–O(2)	83.89 (12)	P(1)–O(4)–C(16)	119.38 (18)
O(1)–P(1)–O(4)	102.84 (12)	P(2)–O(3)–C(26)	121.51 (19)

(2) A similar hypothetical structure has been proposed in: Van Wazer, J. R. *Phosphorus and Its Compounds*; Interscience: New York, 1958; Vol. I, p 414.

(3) A minor contaminant is **5**, which has characteristic IR absorptions at 1040 and 1006 cm⁻¹.

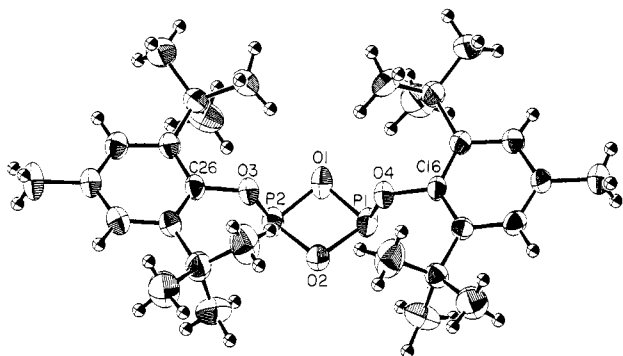


Figure 1. Molecular structure of **3** (50% probability thermal ellipsoids).

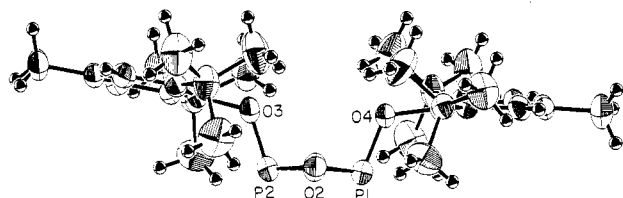
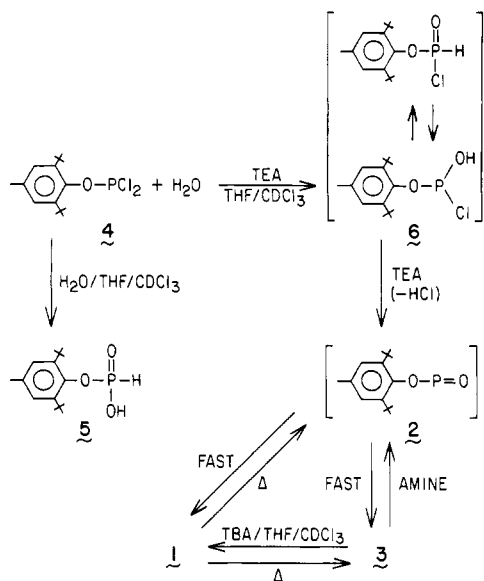


Figure 2. Molecular structure of **3** showing nonplanar P_2O_2 ring and cis configuration.

Scheme I



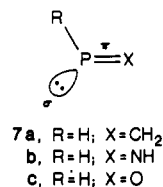
P_3O_3 ring are not all equivalent and range from 1.619 to 1.651 Å. In the dimer, the two exocyclic P—O distances are equivalent, 1.610 ± 0.001 Å. Again, a nonequivalence is observed in two of the three exocyclic P—O distances in the trimer (1.622, 1.635, and 1.621 Å). The P—O—P and O—P—O angles within the dimer are statistically equivalent, while within the trimer, only two of the three angles of each type are statistically significant. Finally, the P_1 — P_2 distance in **3** is 2.476 Å compared to only 2.223 Å for the O_1 — O_2 separation. These distances are consistent with the concept of steric interaction between the exocyclic phenoxy groups. The lengthening of the P_1 — P_2 distance and the shortening of the O_1 — O_2 distance would act to decrease the intramolecular interaction.

The alternating P_2O_2 four-membered ring in **3** is the first example of its type wherein both P atoms are P(III). However, a theoretical determination of the sequence of energies of the frontier orbitals of phosphaaalkenes provides a basis for their dimerization to form $P^{III}_2O_2$ and $P^{III}_2N_2$ rings.⁴ To date, we are unaware of any structure determination that verifies the existence of $P^{III}_2N_2$ rings in the condensed state. A recent paper paper by

Cowley and co-workers, however, establishes the existence in the condensed state of an alternating $P^{III}_2B_2$ four-membered ring.⁵ They determined the X-ray crystal structure of what can be regarded as the head-to-tail dimer of the unknown boraphosphene ($R-B=P-R'$) with $R = \text{mesityl}$ and $R' = 2,2,6,6\text{-tetramethylpiperidino}$ groups. The P_2B_2 ring is planar, the molecule has a center of symmetry, and consequently both the piperidino and mesityl groups adopt mutually trans orientations.

An alternative mechanism has been proposed¹ but our preferred mechanism for the formation of **3** and **1** is shown in Scheme I and is supported by the following observations. When **4** in tetrahydrofuran (THF)/ $CDCl_3$ is treated with incremental amounts of water (2 equiv) and the ^{31}P NMR spectrum monitored, the absorption at 201 ppm due to **4** disappears and an absorption at 1.9 ppm for **5** appears (compared to authentic sample). No intermediate absorptions are observed. When incremental amounts of 1 equiv of water are added to **4** in THF/ $CDCl_3$ in the presence of 2 equiv of triethylamine (TEA), the absorption at 201 ppm decreases, the characteristic doublet and triplet, attributed to **1**,¹ begin to grow, and temporary absorptions at 176.2, 164.7, and 163.9 ppm appear until the addition of all the water is complete, at which time they disappear. The 176.2 ppm absorption is due to **3** (see Experimental Section), while the other two absorptions may be related to **6** or **2**, although it would be difficult to predict where **2** would absorb. **3** is stable in THF/ $CDCl_3$ solution alone but when tributylamine (TBA) is added, **3** is rapidly converted to **1**. This observation suggests that the role of the amine is more than just as an HCl acceptor in the conversion of **4** to **1a**. While it appears that the amine simply dedimerizes **3**, further study is required before additional speculation is merited. When **1** or **3** is examined under FD/MS conditions, an m/e of 266 corresponding to that of **2** is generally observed (in addition to other m/e 's). Thus, when **1** is sublimed, it may actually be thermally cleaved to **2**, an aryl phosphenite, which recombines to form both **1** and **3** on the cold finger. We plan to establish the intermediacy of **2** through other appropriate trapping experiments. An alkyl phosphenite has been detected as a reaction intermediate,⁶ while related or analogous species, e.g., $R-P$,⁷ $R-P=O$,⁷ $R-P=S$,⁸ $(i\text{-Pr})_2N-P=O$,⁹ $ROP=S$,¹⁰ $R_2N-P=S$,¹⁰ and $R-B=O$,¹¹ have been alluded to previously.

If indeed **3** is formed by the dimerization of **2**, certain theoretical implications exist. Schoeller and Niecke⁴ have presented theoretical evidence that species like **7** can react as 1,2 or 1,1 dipoles, with the reactivity depending on the electronegativity of X and the presence of π -donating or π -accepting substituents attached to the $P=X$ system. While **7a** would undergo a head-to-tail [2



+ 2] cycloaddition, **7b** and **7c** would undergo a [2 + 1] cycloaddition.⁴ In **2**, the $=O$ is conducive to [2 + 1] addition while the $Ar-\ddot{O}-$ group, a π -donator on the phosphorus, would favor [2 + 2] addition. Our observation that **2** undergoes head-to-tail [2 + 2] cycloaddition suggests that the $Ar-\ddot{O}-$ group raises the energy of the π -molecular orbital above that of the σ -orbital, which has been influenced little in energy by the $=O$ substituent. Thus,

(5) Arif, A. M.; Cowley, A. H.; Pakulski, M.; Power, J. M. *J. Chem. Soc., Chem. Commun.* **1986**, 889–890.

(6) Fookes, C. J. R.; Gallagher, M. J.; Honegger, H. *J. Chem. Soc., Chem. Commun.* **1978**, 324–325.

(7) Schmidt, U. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 523–528.

(8) Nakayama, S.; Yoshifuji, M.; Okazaki, R.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* **1971**, 1186–1187.

(9) Niecke, E.; Zorn, H.; Drebs, B.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 709–710.

(10) Quin, L. D.; Szweczyk, J. *J. Chem. Soc., Chem. Commun.* **1986**, 844–846.

(11) Pachaly, B.; West, R. *J. Am. Chem. Soc.* **1985**, *107*, 2987–2988.

(4) Schoeller, W. W.; Niecke, E. *J. Chem. Soc., Chem. Commun.* **1982**, 569–570.

the π/π^* frontier molecular orbital interaction (vs. σ/π^*) leads to a [2 + 2] cycloaddition reaction (nonconcerted) product. Theoretical calculations¹² support this conclusion.

Experimental Section

Melting points were obtained on a Mel-Temp apparatus and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 467 spectrometer. Field desorption mass spectra were obtained on a Finnigan MAT 311A mass spectrometer. All ¹H NMR spectra were obtained on a Bruker WH-200 instrument, and the chemical shifts are reported in ppm from internal TMS.

The proton-decoupled ³¹P spectra were acquired on a Bruker HX90E/SXP spectrometer using the standard multinuclear probe head. Samples were run with CDCl₃ as solvent in 10-mm tubes. Chemical shifts were measured relative to an external capillary of 85% aqueous H₃PO₄. Typical conditions: recycle time, 10 s; 90° rf pulse width, 15 μ s; spectral width, 12048 Hz in 8192 points.

Crystals suitable for the X-ray structure were made by recrystallizing **3** from chloroform. The X-ray intensity data (11369 reflections, $2.0^\circ \leq 2\theta \leq 50.0^\circ$, $h, \pm k, \pm l$, 2θ scan) from a single crystal of **3** were recorded on a Syntex P2 four-circle diffractometer at ambient temperature using graphite-monochromated Mo K α radiation. The 2780 reflections with $I > 3.0\sigma(I)$ were corrected for Lorentz, decay, and polarization effects. The initial P and O atom positions were located with MULTAN. All

remaining non-hydrogen atom positions were located by subsequent difference Fourier techniques. All computations were made with the UCLA Crystallographic Package installed on a DEC VAX 8600/750 cluster.

Preparation of 3. **1a** (10 g, 12.5 mmol) is sublimed at 220 °C (1–1.2 kPa) for 4 h. The sublimate (~6 g) is then stirred in diethyl ether (25–30 mL) for 20 min to extract **1a**. Filtration affords 3.2 g (32%) of nearly pure³ product: mp 174–182 °C; IR (Nujol) 1175, 1100, 888, 870, 853 (P–O–P), 772, 755, 730, 720, and 700 cm⁻¹; field desorption/mass spectrometry (FD/MS) m/e 532 (trace of m/e 266); ¹H NMR (CDCl₃) δ 1.48 (s, 36 H), 2.30 (s, 6 H), 7.14 (s, 4 H); ³¹P{¹H} NMR (CDCl₃) 176.5 ppm.

NMR Study. **4** (0.5 g, 1.6 mmol) is placed in a 10-mm NMR tube and dissolved in THF. Sufficient CDCl₃ is added for a lock signal. TEA (0.32 g, 3.2 mmol) is added and the spectrum is taken. Then water (0.028 g, 1.6 mmol, 28 μ L) is added in 7- μ L increments with a microliter syringe. After each addition, the spectrum is run.

Acknowledgment. We thank Perry Matheny for his synthetic assistance and Barbara Bancroft of Texas A&M University for performing the molecular orbital calculations.

Supplementary Material Available: Tables S1, S2, and S3 listing hydrogen atomic parameters, anisotropic thermal parameters, and isotropic thermal parameters (4 pages); table of observed and calculated structure factor amplitudes for **3** (13 pages). Ordering information is given on any current masthead page.

(12) Bancroft, B., private communication, Mar 1986.

Reaction of Bulky Monosubstituted Phosphorus(III) Halides with Disodium Pentacarbonylchromate. Steric and Electronic Factors in the Synthesis of Cr(CO)₅ Complexes of Diphosphenes, Phosphinidenes, Phosphanes, Diphosphanes, and Cyclopolyphosphanes

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Abstract: Reaction of Na₂Cr(CO)₅ with a bulky monosubstituted phosphorus(III) halide, RPCl₂, where R = 2,4,6-Me₃C₆H₂ (Mes), CH₂SiMe₃, CH(SiMe₃)₂, N(SiMe₃)₂, or -OC₆H₂-2,6-*i*-Bu₂-4-Me, leads to at least nine different types of product which may involve diphosphene, phosphinidene, phosphane, diphosphane, and cyclopolyphosphane ligands. The products obtained depend markedly on the size and electronic properties of the substituent on phosphorus. The synthesis and properties of 12 compounds of which 10 have been structurally characterized by X-ray crystallography are described in this paper. IR and ³¹P NMR data are also reported. The compounds are [*trans*-(PMes)₂Cr(CO)₃]₂ (**1a**), [Cr(CO)₅][P(H)Mes]₂ (**2**), [Cr(CO)₅][*cyclo*-(PMes)₃] (**3**), [Cr(CO)₅][*cyclo*-(PCH₂SiMe₃)₄] (**5**), [*trans*-(PCH₂SiMe₃)₂Cr(CO)₃]₂ (**6**), [*trans*-(PCH(SiMe₃)₂)₂Cr(CO)₃]₂ (**7**), [*trans*-(PN(SiMe₃)₂)₂Cr(CO)₃]₂ (**8**), [Cr(CO)₅PN(SiMe₃)₂] (**9**), [*trans*-(Cr(CO)₄)]PN(SiMe₃)₂Cr(CO)₃ (**10**), [Cr(CO)₅(PCl₂OC₆H₂-2,6-*i*-Bu₂-4-Me)] (**11**), and [Cr(CO)₅](POC₆H₂-2,6-*i*-Bu₂-6-Me)] (**12**). Details of the structures of complexes **1a**, **2**, **3**, **5**, and **6** in addition to **11** and **12** are described and discussed in conjunction with those of **7**, **9**, and **10** which have been reported in preliminary publications. Crystal data [Mo K α (λ = 0.710 69 Å)] at 130 K are as follows: **1a**, C₂₈H₂₂Cr₂P₂O₁₀, a = 11.170 (6) Å, b = 16.159 (8) Å, c = 9.260 (5) Å, β = 113.91 (4)°, Z = 2, monoclinic, space group $P2_1/c$, R = 0.0745; **2**, C₂₈H₂₂Cr₂P₂O₁₀·C₆H₁₄, a = 9.008 (4) Å, b = 9.418 (4) Å, c = 11.625 (3) Å, α = 96.77 (3)°, β = 112.21 (3)°, γ = 94.69 (4)°, Z = 1, triclinic, space group $P\bar{1}$, R = 0.052; **3**, C₃₂H₃₃CrP₃O₅, a = 10.507 (6) Å, b = 11.437 (7) Å, c = 14.707 (9) Å, α = 110.95 (4)°, β = 90.49 (5)°, γ = 104.48 (4)°, Z = 2, triclinic, space group $P\bar{1}$, R = 0.045; **5**, C₂₆H₄₄Cr₂P₂O₁₀Si₄, a = 10.322 (4) Å, b = 19.180 (4) Å, c = 11.198 (4) Å, β = 109.79 (2)°, Z = 2, monoclinic, space group $P2_1/c$, R = 0.050; **6**, C₁₈H₂₂Cr₂P₂O₁₀Si₂, a = 6.989 (3) Å, b = 9.226 (4) Å, c = 10.975 (5) Å, α = 106.08 (3)°, β = 93.36 (3)°, γ = 94.58 (3)°, Z = 1, triclinic, space group $P\bar{1}$, R = 0.064; **11**, C₂₀H₂₃CrPO₆Cl₂, a = 13.068 (2) Å, b = 11.426 (3) Å, c = 15.852 (4) Å, β = 93.81 (2)°, Z = 4, monoclinic, space group $P2_1/a$, R = 0.031; **12**, C₂₅H₂₃Cr₂PO₁₁ (at 293 K), a = 9.224 (1) Å, b = 16.549 (2) Å, c = 20.240 (2) Å, α = 73.74 (1)°, β = 80.44 (1)°, γ = 87.50 (1)°, Z = 4 (2 dimers), triclinic, space group $P\bar{1}$, R = 0.056.

Compounds that contain unsupported double bonds between heavier main group elements have been made accessible primarily

through the use of bulky substituents^{3–5} which ensure kinetic stabilization by preventing association and further reaction of the