

Synthesis and Reactivity of Functionalized Rhenium Phosphido Complexes ($\eta^5\text{-C}_5\text{H}_5$)Re(NO)(PPh₃)(PXX'): An Unusual CCl₄ 1,3-Addition Leading to an Exo-Substituted η^4 -Cyclopentadiene Complex

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Received April 18, 1989

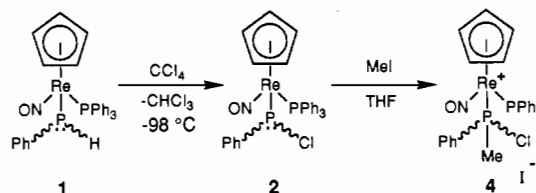
Reaction of the phenylphosphido complex ($\eta^5\text{-C}_5\text{H}_5$)Re(NO)(PPh₃)(PPhH) and CCl₄ (1 equiv, -98 °C) gives the labile chlorophenylphosphido complex ($\eta^5\text{-C}_5\text{H}_5$)Re(NO)(PPh₃)(PPhCl) (**2**, mixture of diastereomers), which is characterized in situ by NMR spectroscopy and methylation to the isolable bis(phosphine) complex [($\eta^5\text{-C}_5\text{H}_5$)Re(NO)(PPh₃)(PPhMeCl)]⁺I⁻. Reaction of P(NMe₂)₃ and either **2** (1.0 equiv) or the dichlorophenylphosphine complex [($\eta^5\text{-C}_5\text{H}_5$)Re(NO)(PPh₃)(PPhCl₂)]⁺CF₃SO₃⁻ (0.5 equiv) gives predominantly [($\eta^5\text{-C}_5\text{H}_5$)Re(NO)(PPh₃)(PPh(P(NMe₂)₂))] ⁺Cl⁻, which is characterized in situ by NMR spectroscopy. Reaction of Li⁺[($\eta^5\text{-C}_5\text{H}_5$)Re(NO)(PPh₃)]⁻ with *t*-BuPCl₂ and P(OPh)₃ gives ($\eta^5\text{-C}_5\text{H}_5$)Re(NO)(PPh₃)(P(*t*-Bu)Cl) (**9**, 72%) and ($\eta^5\text{-C}_5\text{H}_5$)Re(NO)(PPh₃)(P(OPh)₂) (**10**, 57%), respectively. Reaction of **2** and CCl₄ gives the η^4 -cyclopentadiene complex ($\eta^4\text{-C}_5\text{H}_5\text{CCl}_3$)Re(NO)(PPh₃)(PPhCl₂), which exhibits dynamic NMR behavior and is characterized by an X-ray crystal structure (monoclinic, *P*2₁/*c*, *a* = 9.352 (2) Å, *b* = 31.241 (8) Å, *c* = 10.812 (1) Å, β = 102.54 (1)°, *Z* = 4). Reactions of **2**, **9**, and **10** with potential halide abstractors and related reagents are also described.

Introduction

We have had an ongoing interest in the synthesis, structure, dynamic behavior, and reactivity of coordinatively saturated, pyramidal transition-metal phosphido complexes.¹⁻³ As part of this program, we have sought to prepare functionalized phosphido complexes of the general formula L_nM-PXX' (X = alkyl, aryl, or heterosubstituent; X' = heterosubstituent) that might serve as precursors to cationic phosphinidene complexes [L_nM=PX]⁺.^{4,5} Earlier, we reported that the iron phosphido complex ($\eta^5\text{-C}_5\text{Me}_5$)Fe(CO)₂(PCIN(*i*-C₃H₇)₂) can be converted to an unstable but spectroscopically observable species (³¹P NMR, 954 ppm) that was assigned as phosphinidene complex [($\eta^5\text{-C}_5\text{Me}_5$)Fe(CO)₂(=PN(*i*-C₃H₇)₂)]⁺.¹ We thought that replacement of the iron fragment [($\eta^5\text{-C}_5\text{Me}_5$)Fe(CO)₂]⁺ by the better π -donating rhenium fragment⁶ [($\eta^5\text{-C}_5\text{H}_5$)Re(NO)(PPh₃)]⁺ might afford more stable phosphinidene complexes. Hence, we set out to study the synthesis and chemistry of functionalized rhenium phosphido complexes ($\eta^5\text{-C}_5\text{H}_5$)Re(NO)(PPh₃)(PXX').⁷

In this paper, we describe (1) the synthesis and spectroscopic characterization of rhenium chlorophenylphosphido (-PPhCl), phosphinophenylphosphido (-PPh(PX''₃)), chloro-*tert*-butylphosphido (-P(*t*-Bu)Cl), and diphenoxyphosphido (-P(OPh)₂)

Scheme I. Synthesis and Methylation of the Chlorophenylphosphido Complex ($\eta^5\text{-C}_5\text{H}_5$)Re(NO)(PPh₃)(PPhCl) (**2**)



complexes, (2) selected reactions with alkylating agents, potential halide abstractors, and other reagents, (3) an unusual 1,3-addition of CCl₄ to the chlorophenylphosphido complex that affords an exo-substituted η^4 -cyclopentadiene bis(phosphine) complex, and (4) the crystal structure of this complex.

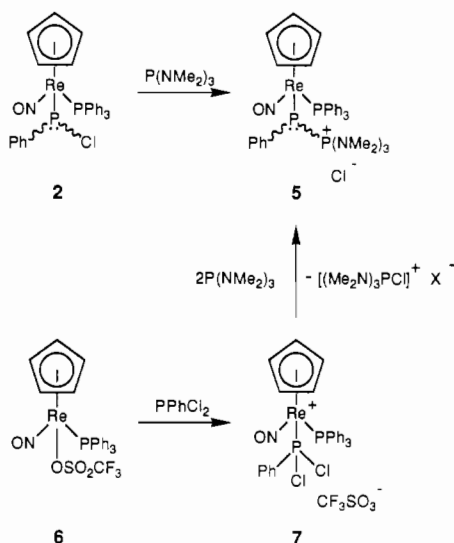
Results

1. Synthesis and Methylation of a Chlorophenylphosphido Complex. Carbon tetrachloride has frequently been used to convert phosphorus-hydrogen bonds to phosphorus-chlorine bonds.⁸ Accordingly, reaction of the previously reported phenylphosphido complex ($\eta^5\text{-C}_5\text{H}_5$)Re(NO)(PPh₃)(PPhH) (**1**; ca. 50:50 mixture of diastereomers)^{3b,9} and CCl₄ (1.0-1.2 equiv, THF, -98 °C) was monitored by ³¹P NMR. A spectrum recorded at -90 °C showed that the two resonances of each diastereomer of **1** (+24.22 and -91.84 (s, PPh₃ and PPhH); +18.72 and -110.68 (d, ¹J_{PP} = 15.3 Hz, PPh₃ and PPhH)) had been replaced by two new sets of doublets: (a) 199.64 and 16.13 ppm (d, ¹J_{PP} = 21.2 Hz, PPhCl and PPh₃); (b) 195.42 and 17.66 ppm (d, ¹J_{PP} = 31.7 Hz, PPhCl and PPh₃). No ¹J_{PH} couplings, which are typically 250-600 Hz, were observed for any resonance. Downfield ³¹P NMR chemical shifts have previously been noted for phosphido ligands with electronegative substituents.¹⁰ Hence, the new resonances were provisionally assigned to two diastereomers (**a**, **b**) of the chlorophenylphosphido complex ($\eta^5\text{-C}_5\text{H}_5$)Re(NO)(PPh₃)(PPhCl) (**2**, Scheme I).

The **2a/2b** diastereomer ratio was ca. 80:20 in the initial -90 °C spectrum. When the sample was warmed to -60 °C, the ratio reversed to ca. 40:60.¹¹ Also, a minor side product (**3**, ca. 10%) was evident at -90 °C. At -60 °C, additional conversion to **3** began. When an analogous reaction was conducted at -98 °C with 2 equiv of CCl₄, only **3** formed. The isolation and charac-

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- (4) Reviews of transient or thermally unstable phosphinidene complexes: (a) Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 275. (b) Cowley, A. H.; Barron, A. R. *Acc. Chem. Res.* **1988**, *21*, 81.
- (5) First isolable phosphinidene complexes: Hitchcock, P. B.; Lappert, M. F.; Leung, W.-P. *J. Chem. Soc., Chem. Commun.* **1987**, 1282.
- (6) A variety of theoretical and experimental data support this π -basicity order. For example, Fe=C_α rotational barriers in iron alkylidene complexes [($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)(PPh₃)(=CHR)]⁺ are ca. 8 kcal/mol: Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411 (see ref 49). Studabaker, W. B. Ph.D. Thesis, The University of North Carolina, Chapel Hill, NC, 1986, p 97. The Re=C_α rotational barriers in analogous rhenium alkylidene complexes [($\eta^5\text{-C}_5\text{H}_5$)Re(NO)(PPh₃)(=CHR)]⁺ are 15-21 kcal/mol: Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865. Kiel, W. A.; Lin, G.-Y.; Bodner, G. S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 4958.
- (7) There is an extensive literature on functionalized phosphido complexes. Some recent studies with objectives similar to our own include: (a) Stasunik, A.; Wilson, D. R.; Malisch, W. *J. Organomet. Chem.* **1984**, *270*, C18. (b) Malisch, W.; Angerer, W.; Cowley, A. H.; Norman, N. C. *J. Chem. Soc., Chem. Commun.* **1985**, 1811. (c) Bohle, D. S.; Jones, T. C.; Rickard, C. E. F.; Roper, W. R. *Organometallics* **1986**, *5*, 1612. (d) Bohle, D. S.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R. *J. Organomet. Chem.* **1988**, *353*, 355.

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- (9) Buhro, W. E. Ph.D. Thesis, UCLA, 1985.
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- (11) We assume that the relative ³¹P NMR integrals of diastereomeric complexes reasonably approximate the diastereomer ratio.

Scheme II. Syntheses of the P(NMe₂)₃/Phosphinidene Adduct [(η⁵-C₅H₅)Re(NO)(PPh₃)(P̄Ph(P(NMe₂)₃))] + Cl⁻ (5)

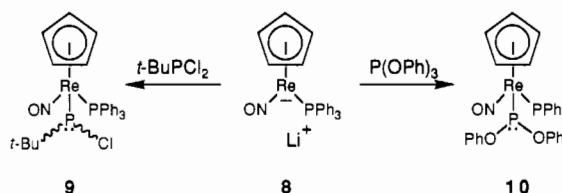
terization of 3 is described below. Importantly, when the radical inhibitor duroquinone (3 equiv) was added after the addition of 2 to CCl₄, formation of 3 was suppressed. No conversion of 1 h at -25 °C. Finally, complex product mixtures formed when *N*-chlorosuccinimide or *tert*-butyl hypochlorite was used in place of CCl₄.

Complex 2 was not sufficiently stable to be isolated. Hence, it was generated in THF-*d*₈ and further characterized in situ by ¹H and ¹³C{¹H} NMR. Data are summarized in Table I. Features were similar to those reported previously for the dialkyl- and diarylphosphido complexes (η⁵-C₅H₅)Re(NO)(PPh₃)(P̄R₂).² Integration of the phenyl and η⁵-C₅H₅ ligand ¹H NMR resonances indicated a ca. 90% yield of 2. One equivalent of CHCl₃ also formed (¹H NMR, δ 8.26 (s); ¹³C{¹H} NMR, δ 9.85 (s) ppm; chemical shifts were verified by independent spectra of CHCl₃ in THF-*d*₈).

We sought chemical evidence to support the formulation of 2. The phosphido ligand in the symmetrically substituted complex (η⁵-C₅H₅)Re(NO)(PPh₃)(P̄R₂) has previously been shown to be exceptionally nucleophilic.^{2,3} Accordingly, reaction of 2 and CH₃I (THF, -98 °C followed by warming) gave the bis(phosphine) complex [(η⁵-C₅H₅)Re(NO)(PPh₃)(PPhMeCl)]⁺I⁻ (4) as a (53 ± 2):(47 ± 2) mixture of diastereomers (Scheme I). Workup gave the solvate 4·0.167THF as a thermally stable, moderately air-sensitive yellow powder (63%), which was characterized by NMR and IR spectroscopy (Table I) and microanalysis (C, H, Cl, I). Spectral features were similar to those reported earlier for related cationic bis(phosphine) complexes.^{2,3} The new phosphorus-bound methyl group was evidenced by two doublets (one for each diastereomer) in the ¹³C{¹H} NMR spectrum, and a single doublet (accidental degeneracy) in the ¹H NMR spectrum. Crystallization of 4·0.167THF from CH₂Cl₂/ether gave gold-colored nuggets with a correct microanalysis for unsolvated 4, but a ¹H NMR spectrum indicated the presence of a *third* component (in CD₂Cl₂; δ 5.54 (s, C₅H₅), 2.28 (d, *J*_{HP} = 9.5 Hz, CH₃); ca. 29%), possibly the result of internal chloride/iodide metathesis. We subsequently noted the slow formation of this species in CH₂Cl₂ solutions of 4·0.167THF.

2. Generation of a P(NMe₂)₃/Phosphinidene Complex Adduct.

Having established the reactivity of the chlorophenylphosphido complex 2 toward electrophiles, we next sought to examine reactions of 2 and nucleophiles. Hence, 2 and P(NMe₂)₃ (3 equiv) were combined in THF-*d*₈ at -78 °C. The sample was slowly warmed and monitored by ¹H, ³¹P, and ¹³C{¹H} NMR spectroscopy. The complete disappearance of 2 required several hours at -25 °C, and the major product (ca. 55% based upon ¹H NMR integration) exhibited NMR properties consistent with the formulation [(η⁵-C₅H₅)Re(NO)(PPh₃)(P̄Ph(P(NMe₂)₃))] + Cl⁻ (5, Scheme II). In particular, three resonances were observed in the

Scheme III. Reactions of the Rhenium "Anion" Li⁺[(η⁵-C₅H₅)Re(NO)(PPh₃)]⁻ (8) and Phosphorus Electrophiles

³¹P{¹H} NMR spectrum. Two of them (85.26, P(NMe₂)₃; -59.51, P̄Ph) were coupled with a large ¹*J*_{PP} of 436 Hz, indicative of a phosphorus-phosphorus bond.¹² Only one diastereomer appeared to be present, and a proton-coupled ³¹P NMR spectrum showed no ¹*J*_{HP}.

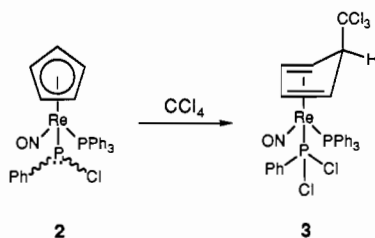
Complex 5 can be considered an adduct of P(NMe₂)₃ and phosphinidene complex [(η⁵-C₅H₅)Re(NO)(PPh₃)(=P̄Ph)] + Cl⁻. Hence, a higher yield synthesis was sought. The triflate complex (η⁵-C₅H₅)Re(NO)(PPh₃)(OSO₂CF₃) (6)¹³ has previously been shown to readily react with phosphines to give triflate salts of cationic bis(phosphine) complexes.^{2c} Hence, 6 and PPhCl₂ were analogously reacted to give the dichlorophenylphosphine complex [(η⁵-C₅H₅)Re(NO)(PPh₃)(PPhCl₂)]⁺CF₃SO₃⁻ (7), which was isolated as air-stable yellow crystals (80%, Scheme II). Complex 7 was characterized analogously to the bis(phosphine) complex 4 (Table I and Experimental Section).

Complex 7 was next combined with P(NMe₂)₃ (2 equiv) in CD₂Cl₂ at -78 °C (Scheme II). The sample was slowly warmed and monitored by ¹H, ³¹P, and ¹³C{¹H} NMR spectroscopy. Complete reaction of 7 required several hours at -25 °C. Complex 5 formed in ca. 70% yield (¹H NMR), and [(Me₂N)₃PCl]⁺X⁻ (X⁻ = Cl⁻ or CF₃SO₃⁻)¹⁴ was the only other major product. Solutions of 5 showed no sign of decomposition over the course of 9 days at room temperature, but all isolation attempts were unsuccessful. When 7 was treated with 1 equiv of P(NMe₂)₃, only ca. 50% was consumed.

3. Reactions of Li⁺[(η⁵-C₅H₅)Re(NO)(PPh₃)]⁻ and Phosphorus Electrophiles. The rhenium "anion" Li⁺[(η⁵-C₅H₅)Re(NO)(PPh₃)]⁻ (8) has previously been shown to react with a variety of electrophiles to give neutral adducts (η⁵-C₅H₅)Re(NO)(PPh₃)(X).^{15,16} Hence, its utility as a precursor to functionalized phosphido complexes was evaluated. Reaction of 8 and *t*-BuPCl₂ (THF, -78 °C followed by warming) was monitored by ³¹P{¹H} NMR spectroscopy. The initial spectrum, recorded at -60 °C, exhibited two sets of resonances (area ratios ca. 85:15): 208 and 20 ppm (d, ²*J*_{PP} = 63 Hz, *t*-BuPCl and PPh₃) and 262 and 23 ppm (s, *t*-BuPCl and PPh₃). These were assigned as two diastereomers (a, b) of the *tert*-butylchlorophosphido complex (η⁵-C₅H₅)Re(NO)(PPh₃)(P̄(*t*-Bu)Cl) (9; Scheme III). When the sample was warmed to room temperature, the 9a/9b ratio became ca. 50:50. A decomposition product slowly appeared, which after 3 days comprised ca. 50% of the reaction mixture. The ³¹P{¹H} NMR spectrum of this material showed two resonances (THF, -60 °C: 85.11 (d, *J*_{PP} = 26 Hz), 13.61 ppm (d, *J*_{PP} = 26 Hz)). The one at lower field, likely P(*t*-Bu)Cl-derived, exhibited a large ¹*J*_{PH} (478 Hz) value indicative of a phosphorus-hydrogen bond.

The preceding reaction was repeated on a preparative scale. Workup gave 9 as a ≥90% pure, air-sensitive, dull red powder (ca. 72%). Further purification attempts gave poor recoveries of

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 (14) (a) Appel, R.; Gläsel, U. *Chem. Ber.* **1980**, *113*, 3511. (b) Note that the cationic products of the reaction of 7 and P(NMe₂)₃ may be associated with either Cl⁻ or CF₃SO₃⁻ counteranions.
 (15) Crocco, G. L.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 6110.
 (16) (a) Crocco, G. L.; Young, C. S.; Lee, K. E.; Gladysz, J. A. *Organometallics* **1988**, *7*, 2158. (b) Lee, K. E.; Gladysz, J. A. *Polyhedron* **1988**, *7*, 2209.

Scheme IV. Synthesis of the Exo-Substituted η^4 -Cyclopentadiene Complex (η^4 -C₅H₅CCl₃)Re(NO)(PPh₃)(PPhCl₂) (**3**)

material of lower purity. Benzene and THF solutions of **9** decomposed within a few hours at room temperature, and CH₂Cl₂ solutions were considerably less stable. Spectroscopic characterization of **9** is summarized in Table I, and a mass spectrum exhibited a parent ion.

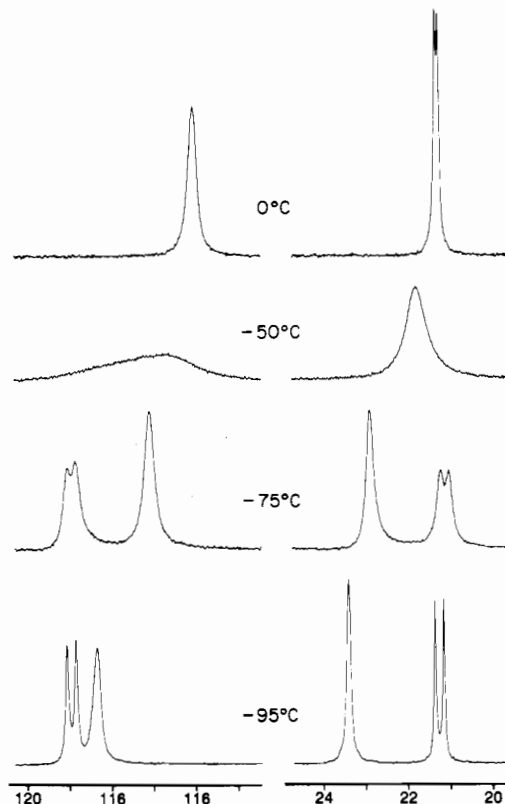
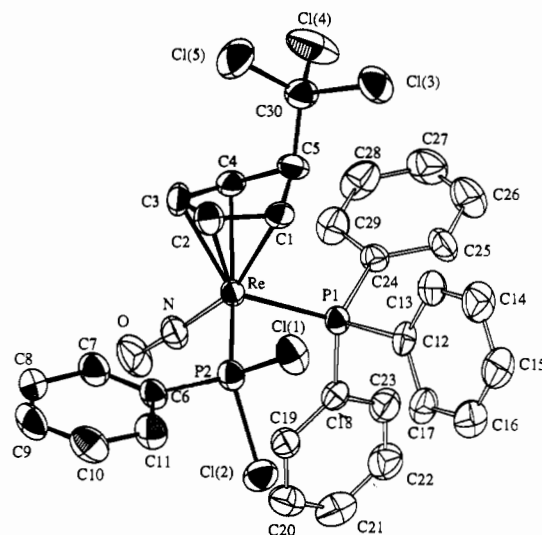
The ¹H and ¹³C{¹H} NMR spectra of one of the diastereomers of **9** exhibited broadened η^5 -C₅H₅ and *t*-Bu resonances (Table I). Furthermore the P(*t*-Bu)Cl ³¹P{¹H} NMR resonance (32 MHz, THF, -80 °C: 208.13 ppm (d, *J*_{PP} = 63.3 Hz)) was resolved at higher fields into two doublets of unequal intensity (121 MHz, C₆D₆, 30 °C: 211.39 (d, *J*_{PP} = 65.6 Hz, major), 211.32 ppm (d, *J*_{PP} = 65.7 Hz, minor)). No other resonance was similarly affected. These observations suggest that the interconversion of rotamers of one diastereomer is approaching the slow-exchange regime.

Triaryl phosphites have been previously observed to undergo nucleophilic substitution with carbanionic reagents.¹⁷ Hence, **8** was treated with P(OPh)₃ (THF, -78 °C followed by warming). Workup gave the crude diphenoxyphosphido complex (η^5 -C₅H₅)Re(NO)(PPh₃)(P(OPh)₂) (**10**, Scheme III) as an air-sensitive orange powder (57%, ca. 95% pure). Orange crystals of analytically pure **10**·0.5(hexane) were obtained from benzene/hexane, but substantial decomposition accompanied crystallization. Complex **10**·0.5(hexane) was characterized as described for the other new compounds above. The mass spectrum exhibited a parent ion, and the P(OPh)₂ ligand exhibited the expected low-field ³¹P NMR chemical shift (337.34 ppm). The diastereotopic OPh groups gave separate sets of sharp resonances in the ambient-temperature ¹³C{¹H} NMR spectrum.

4. Conversion of the Chlorophenylphosphido Complex 2 to an Exo-Substituted η^4 -Cyclopentadiene Complex. Workup of the reaction of **1** with 2.0 equiv of CCl₄ (vide supra) gave the solvate 3·0.167C₆H₆ (65%) as an orange air-stable powder (Scheme IV). Crystallization from cold CH₂Cl₂ gave unsolvated **3**. Microanalyses of both samples (C, H, Cl) suggested that **3** was derived from the addition of CCl₄ to **2** (MW 841). We initially thought that **3** might somehow form via an intermediate phosphinidene complex and hence undertook an extensive study of its spectroscopic properties (Table I) in an attempt to establish its structure.

First, the IR ν_{NO} , ³¹P NMR PPh₃ chemical shift, and solubility data suggested a neutral complex. The ¹H and ¹³C NMR spectra clearly showed that **3** did not retain a simple cyclopentadienyl ligand. In particular, the ambient-temperature ¹H NMR spectrum (Table I) showed five distinct one-hydrogen resonances between δ 5.44 and 2.66. These decoalesced to 10 resonances in a spectrum recorded at -80 °C: δ 5.61, 5.46, 5.32, 5.15, 4.12, 3.55, 3.02, 2.82, 1.83, 0.93 (all br s, 0.5 H). The ambient-temperature ¹³C{¹H} NMR spectrum exhibited six non-phenyl carbon resonances. A ¹H-coupled ¹³C NMR spectrum showed that five of these carbons possessed one directly bound hydrogen (¹*J*_{CH} = 148–184 Hz).⁹ These were provisionally assigned to the original η^5 -C₅H₅ unit. The sixth resonance did not exhibit a ¹*J*_{CH} coupling but did show longer range coupling (21 Hz) to a single hydrogen. This carbon was presumed to be CCl₄-derived.

Dynamic behavior was also observed in variable-temperature ³¹P{¹H} NMR spectra of **3**, as shown in Figure 1. Data at the -95 °C low-temperature limit (ppm, CD₂Cl₂): 118.99 (d, *J*_{PP} = 26.8 Hz, PPhCl₂), 118.36 (br s, PPhCl₂), 23.44 (s, PPh₃), 21.25

**Figure 1.** Variable-temperature ³¹P{¹H} NMR spectra of (η^4 -C₅H₅CCl₃)Re(NO)(PPh₃)(PPhCl₂) (**3**) in CD₂Cl₂.**Figure 2.** Molecular structure of (η^4 -C₅H₅CCl₃)Re(NO)(PPh₃)(PPhCl₂) (**3**).

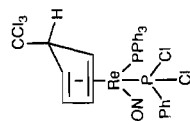
(d, *J*_{PP} = 26.9 Hz, PPh₃). Coalescence temperatures were estimated from Figure 1 (-50, -62 °C) and gave $\Delta G^\ddagger = 9.7 \pm 0.3$ kcal/mol.

The EI mass spectrum of **3** did not give a parent ion, but fragments corresponding to (η^5 -C₅H₅)Re(NO)(PPh₃)(Cl), PPhCl₂, and CCl₃ were prominent. The FAB mass spectrum showed a weak cluster corresponding to the anticipated molecular weight (2 + CCl₄).

Finally, recourse was made to crystallography. X-ray data were collected on unsolvated **3** as summarized in Table II (see supplementary material for full version). Refinement, described in the Experimental Section, yielded the structure shown in Figure 2. Atomic coordinates and selected bond lengths and angles are listed in Tables III–V. Tables of anisotropic thermal parameters, calculated and observed structure factors, and the remaining bond lengths and angles are given in the supplementary material. Figure 2 shows that **3** is an exo-substituted η^4 -cyclopentadiene bis-

Table I. Spectroscopic Characterization of the New Rhenium Complexes

complex	IR (KBr), cm ⁻¹	¹ H NMR, ^a δ	³¹ P{ ¹ H} NMR, ^b ppm	¹³ C{ ¹ H} NMR, ^c ppm
	7.75-6.95 (m, 18 H), 6.62 (br s, 1 H), 6.00 (br s, 1 H), 5.30 (s, 0.75 C ₃ H ₅ , 2a), 5.09 (s, 0.25 C ₃ H ₅ , 2b) ^{d,e}	199.64 (d, <i>J</i> _{PP} = 21.2, PPhCl, 2a), 195.42 (d, <i>J</i> _{PP} = 31.7, PPhCl, 2b), 17.66 (d, <i>J</i> _{PP} = 31.7, PPh ₃ , 2b), 16.13 (d, <i>J</i> _{PP} = 21.2, PPh ₃ , 2a) ^{d,e}	PPh at 151.98 (d, <i>J</i> = 57.4), 136.00 (br s), 134.40 (br s), 132.37 (br s), 131.37 (br s), 130.92 (s), 129.77 (d, <i>J</i> = 25.6), 128.92 (br s), 127.70 (d, <i>J</i> = 28.7); C ₃ H ₅ at 94.22 (s, 2a), 93.97 (s, 2b) ^{d,e}	
	3284 w, 3053 w, 2931-2852 w, ν_{NO} 1649 vs, 1587 w, 1574 w, 1480 m, 1469 m, 1454 m, 1435 s, 1354 m, 1174 w, 1158 w, 1092 m, 1070 w, 1028 w, 1011 w, 999 w, 993 w, 922 w, 829 m, 821 m, 800 w, 745 m, 694 s, 619 w	7.82-7.52 (m, 6 H), 7.10-6.98 (m, 9 H), 5.20-4.80 (br s, 0.5 C ₃ H ₅), 4.78 (s, 0.5 C ₃ H ₅), 1.70 (br d, <i>J</i> _{HP} = 13.9, 0.5 C ₄ H ₉) ^{h,i} , 1.50 (d, <i>J</i> _{HP} = 11.7, 0.5 C ₄ H ₉) ^{h,i}	262.01 (s, P(<i>i</i> -Bu)Cl, 9b), 208.13 (d, <i>J</i> _{PP} = 63.3, P(<i>i</i> -Bu)Cl, 9a), 23.14 (s, PPh ₃ , 9b), 20.01 (d, <i>J</i> _{PP} = 63.3, PPh ₃ , 9a) ^j	PPH ₃ at 136.04 (d, <i>J</i> = 54.1, <i>i</i>), 134.24 (d, <i>J</i> = 11.0, <i>o</i> , 9a), 134.19 (d, <i>J</i> = 10.4, <i>o</i> , 9b), 130.32 (d, <i>J</i> = 2.3, 9a), 128.55 (d, <i>m</i> , 9b); C ₃ H ₅ at 93.24 (br d, <i>J</i> = 5.8), 91.86 (d, <i>J</i> = 1.0); CH ₃ at 31.02 (br d, <i>J</i> = 15.5), 29.14 (d, <i>J</i> = 20.7) ^{h,i,k}
	3110 w, 3057 m, 3029 w, 2957 m, 2857 m, ν_{NO} 1657 vs, 1592 s, 1487 s, 1481 s, 1435 s, 1330 w, 1311 w, 1284 m, 1233 s, 1199 s, 1160 m, 1108 w, 1090 m, 1071 m, 1022 m, 997 m, 901 m, 851 s, 835 s, 822 s, 771 m, 756 s, 749 s, 690 s, 669 s, 604 m	7.65-6.85 (m, 20 H), 5.31 (s, C ₃ H ₅), 2.65 (d, <i>J</i> _{HP} = 9.3, 6 CH ₃) ^{l,m}	85.12 (dd, <i>J</i> _{PP} = 456.4, ³ <i>J</i> _{PP} = 32.4, P(NMe ₂) ₃), 11.54 (dd, ² <i>J</i> _{PP} = 24.0, ³ <i>J</i> _{PP} = 32.5 Hz, PPh ₃), -57.06 (dd, <i>J</i> _{PP} = 456.4, ² <i>J</i> _{PP} = 24.0, PPh) ^{l,m,n}	PPh at 138.84 (dd, <i>J</i> = 20.6, 11.2, <i>o</i>), 131.96 (d, <i>J</i> = 1.8, <i>p</i>), 128.63 (d, <i>J</i> = 8.6, <i>m</i>); PPh ₃ at 134.19 (d, <i>J</i> = 34.6, <i>i</i>), 133.68 (d, <i>J</i> = 12.2, <i>o</i>), 131.17 (d, <i>J</i> = 1.5, <i>p</i>), 128.82 (d, <i>J</i> = 10.4, <i>m</i>); C ₃ H ₅ at 91.83 (s), 6 CH ₃ at 38.96 (d, <i>J</i> = 4.6) ^{l,m}
	3110 w, 3057 m, 3029 w, 2957 m, 2857 m, ν_{NO} 1657 vs, 1592 s, 1487 s, 1481 s, 1435 s, 1330 w, 1311 w, 1284 m, 1233 s, 1199 s, 1160 m, 1108 w, 1090 m, 1071 m, 1022 m, 997 m, 901 m, 851 s, 835 s, 822 s, 771 m, 756 s, 749 s, 690 s, 669 s, 604 m	7.53-7.46 (m, 6 H), 7.38-7.35 (m, 9 H), 7.05-6.94 (m, 4 H), 6.77-6.74 (m, 4 H), 6.47 (d, <i>J</i> _{HH} = 8.0, 2 H), 5.24 (s, C ₃ H ₅), 1.30-1.28 (m, 0.5 of 4 CH ₂ , hexane solvate), 0.88 (t, <i>J</i> _{HH} = 6.5, 0.5 of 2 CH ₃ , hexane solvate) ^{d,m}	337.74 (d, <i>J</i> _{PP} = 26.2, P(OPh) ₂), 18.28 (d, <i>J</i> _{PP} = 26.2, PPh ₃) ^{d,p}	P(OPh) ₂ at 160.88 (d, <i>J</i> = 5.2, <i>i</i>), 159.91 (d, <i>J</i> = 7.4, <i>i</i>), 129.34 (s, <i>m</i>), 129.26 (s, <i>m</i>), 121.90 (s, <i>p</i>), 121.17 (s, <i>p</i>), 120.15 (d, <i>J</i> = 10.5, <i>o</i>), 119.95 (d, <i>J</i> = 9.4, <i>o</i>); PPh ₃ at 137.09 (d, <i>J</i> = 54.5, <i>i</i>), 134.65 (d, <i>J</i> = 10.4, <i>o</i>), 130.88 (d, <i>J</i> = 1.6, <i>p</i>), 128.98 (d, <i>J</i> = 10.4, <i>m</i>); C ₃ H ₅ at 91.84 (s); hexane solvate at 32.47 (s), 23.46 (s), 14.40 (s) ^{d,m}
	3045-2690 m, 2889 m, ν_{NO} 1709 vs, 1586 w, 1480 m, 1435 s, 1414 m, 1357 w, 1312 w, 1298 w, 1180 w, 1159 w, 1092 s, 1074 w, 997 m, 906 m, 878 m, 842 m, 761 m, 751 m, 741 s, 697 s, 690 s, 617 w, 607 w	7.60-7.46 (m, 14 H), 7.35-7.17 (m, 6 H), 5.78 (s, 0.47 C ₃ H ₅), 5.47 (s, 0.53 C ₃ H ₅), 3.70-3.65 (m, 0.167 of 4 H, THF), 2.64 (d, <i>J</i> _{HP} = 8.0, CH ₃), 1.84-1.79 (m, 0.167 of 4 H, THF) ^{l,m}	82.67 (d, <i>J</i> _{PP} = 17.0, PPhMeCl), 79.78 (d, <i>J</i> _{PP} = 16.5, PPhMeCl), 10.90 (d, <i>J</i> _{PP} = 17.1, PPh ₃), 9.81 (d, <i>J</i> _{PP} = 16.5, PPh ₃) ^{m,q}	PPH ₃ at 139.69 (d, <i>J</i> = 55.6, <i>i</i>), 137.42 (d, <i>J</i> = 54.6, <i>i</i>), 133.73 (d, <i>J</i> = 11.5, <i>o</i>), 132.21 (br s, <i>p</i>), 129.79 (d, <i>J</i> = 10.5, <i>m</i>), 129.74 (d, <i>J</i> = 11.5, <i>m</i>); PPhMeCl at 133.10 (d, <i>J</i> = 4.2, <i>o</i>), 133.10 (d, <i>J</i> = 4.2, <i>o</i>), 132.44 (d, <i>J</i> = 3.2, <i>o</i>), 132.37 (d, <i>J</i> = 2.0, <i>p</i>), 132.31 (s, <i>p</i>), 129.50 (d, <i>m</i>); C ₃ H ₅ at 129.15 (d, <i>J</i> = 12.6, <i>m</i>), 30.59 (d, <i>J</i> = 32.5, CH ₃), 28.09 (d, <i>J</i> = 33.5, CH ₃); C ₃ H ₅ at 95.00 (s), 94.37 (s); THF solvate at 68.14 (s), 25.97 (s) ^{l,m}
	3105 m, 3060 m, ν_{NO} 1741 vs, 1585 w, 1573 w, 1481 m, 1437 s, 1422 m, 1269 vs, 1224 m, 1186 m, 1162 s, 1148 s, 1092 s, 1031 s, 1016 m, 998 m, 867 m, 752 m, 708 m, 694 s, 636 s	7.79-7.06 (m, 20 H), 5.68 (s, C ₃ H ₅) ^{l,m}	108.46 (d, <i>J</i> _{PP} = 18.5, PPhCl ₂), 9.55 (d, <i>J</i> _{PP} = 18.5, PPh ₃) ^j	PPHCl ₂ at 140.25 (d, <i>J</i> = 54.1, <i>i</i>), 134.12 (d, <i>J</i> = 1.9, <i>o</i>), 129.78 (d, <i>J</i> = 1.6, <i>m</i>), 129.58 (s, <i>p</i>); PPh ₃ at 133.82 (d, <i>J</i> = 11.0, <i>o</i>), 132.64 (d, <i>J</i> = 2.6, <i>p</i>), 131.99 (d, <i>J</i> = 58.6, <i>i</i>), 129.99 (d, <i>J</i> = 11.0, <i>m</i>); C ₃ H ₅ at 96.21 (s) ^{l,m}



3

3054 w, 2938 w, ν_{NO} 1656 vs, 1586 w, 7.75–7.67 (m, 2 H), 7.51–7.36 (m, 18 H), 7.35 (s, 1 H), 0.167 (1360 w, 1312 m, 1210 w, 1184 w, 1158 w, 1087 s, 1063 w, 1051 w, 1042 w, 1027 w, 998 w, 988 w, 931 m, 834 m, 794 m, 744 s, 731 s, 694 s, 685 s, 653 m, 628 m, 616 w, 116.04 (br s, PPhCl₂), 21.31 (d, J_{PP} = 8.5, PPh₃)^{16a}

PPhCl₂ at 143.84 (d, J = 38.9, i), 131.74 (d, J = 1.5, i), 129.56 (d, J = 16.4, o), 128.41 (d, J = 10.2, m); PPh₃ at 134.70 (dd, J = 50.2, 1.6, i), 133.84 (d, J = 11.3, o), 130.53 (d, J = 1.7, p), 128.60 (d, J = 10.3, m); CCl₃ at 115.51 (dd, J = 20.5, 9.2); C₃H₅CCl₃ at 82.19 (s), 81.32 (s), 72.16 (dd, J = 10.0, 8.6), 45.14 (dd, J = 15.4, 2.6), 44.22 (s)^{16m}

^a At 300 MHz and referenced to internal SiMe₄; all couplings are in Hz. ^b At 32 MHz unless noted and referenced to external H₃PO₄; all couplings are in Hz. ^c At 75 MHz and referenced to internal SiMe₄; all couplings are to ³¹P and are in Hz; assignments of resonances to phenyl carbons are made as described in Table I of: **Buhro, W. E.; Georgiou, S.; Fernández, J. M.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A. *Organometallics* 1986, 5, 956.** ^d In THF-*d*₆. ^e At -80 °C. ^f In THF. ^g At -85 °C. ^h In C₆D₆. ⁱ At 30 °C. ^j High-field line of doublet obscured. ^k The C(CH₃)₃ carbon was not observed. ^l In CD₂Cl₂. ^m At ambient probe temperature. ⁿ At 121 MHz. ^o Ipso carbon resonance not observed. ^p At -29 °C. ^q In CH₂Cl₂. ^r At -25 °C. ^s At 0 °C.

Table II. Summary of Crystallographic Data for (η^4 -C₅H₅CCl₃)Re(NO)(PPh₃)(PPhCl₂) (3)

mol formula =	$T = 15$ °C
C ₃₀ H ₂₅ Cl ₅ NO ₂ Re	$\rho_{\text{calcd}} = 1.811$ g/cm ³
fw = 840.9	$\lambda = 0.71069$ Å
space group = $P2_1/c$	(monochromated)
$a = 9.352$ (2) Å	$\mu = 45.597$ cm ⁻¹
$b = 31.241$ (8) Å	min abs cor = 0.793
$c = 10.812$ (1) Å	max abs cor = 0.983
$\beta = 102.54$ (1)°	$R(F_o) = 0.042$
$V = 3083.7$ Å ³	$R_w(F_o) = 0.052$
$Z = 4$	

Table III. Atomic Coordinates of (η^4 -C₅H₅CCl₃)Re(NO)(PPh₃)(PPhCl₂) (3)^a

atom	x	y	z	10 ⁴ U_{eq} , Å ²
Re	0.15410 (4)	0.12562 (1)	0.24536 (3)	282 (2)
Cl1	0.16769 (33)	0.02870 (9)	0.06205 (25)	490 (18)
Cl2	0.35127 (29)	0.01689 (9)	0.33916 (28)	486 (18)
Cl3	0.05496 (34)	0.19152 (10)	-0.21817 (25)	550 (20)
Cl4	0.03003 (54)	0.26130 (11)	-0.04844 (31)	858 (30)
Cl5	-0.19446 (36)	0.19595 (16)	-0.10524 (34)	896 (30)
P1	0.40240 (26)	0.14366 (8)	0.23557 (22)	289 (14)
P2	0.17028 (28)	0.05187 (8)	0.23922 (24)	338 (15)
O	0.16333 (98)	0.13401 (28)	0.52181 (69)	624 (64)
N	0.16210 (90)	0.12946 (28)	0.41168 (76)	400 (56)
C1	0.07061 (102)	0.13218 (28)	0.03261 (94)	349 (62)
C2	-0.04622 (108)	0.12195 (37)	0.09390 (102)	442 (69)
C3	-0.06225 (111)	0.15488 (47)	0.17164 (100)	568 (83)
C4	0.04813 (107)	0.18721 (34)	0.16060 (85)	380 (63)
C5	0.08949 (111)	0.18085 (31)	0.03473 (87)	368 (63)
C6	0.02849 (104)	0.01952 (30)	0.28379 (89)	338 (60)
C7	-0.06572 (114)	0.03991 (36)	0.34997 (101)	448 (72)
C8	-0.17360 (115)	0.01567 (38)	0.38973 (105)	474 (76)
C9	-0.18915 (120)	-0.02757 (39)	0.36075 (106)	503 (79)
C10	-0.09787 (141)	-0.04700 (37)	0.29540 (115)	552 (85)
C11	0.01230 (122)	-0.02402 (34)	0.25644 (106)	463 (76)
C12	0.47034 (99)	0.11136 (33)	0.11605 (88)	350 (61)
C13	0.41898 (113)	0.11869 (36)	-0.01083 (94)	434 (70)
C14	0.46126 (135)	0.09321 (44)	-0.09924 (106)	572 (86)
C15	0.55745 (134)	0.05939 (40)	-0.06188 (112)	551 (85)
C16	0.60940 (130)	0.05188 (34)	0.06475 (113)	497 (80)
C17	0.56742 (113)	0.07723 (35)	0.15525 (103)	431 (71)
C18	0.53904 (97)	0.13463 (30)	0.38322 (86)	322 (59)
C19	0.51131 (110)	0.10836 (32)	0.47786 (94)	382 (64)
C20	0.61982 (129)	0.10059 (37)	0.58639 (100)	487 (77)
C21	0.75243 (126)	0.12061 (41)	0.60320 (109)	545 (81)
C22	0.78038 (122)	0.14821 (43)	0.51091 (111)	551 (82)
C23	0.67509 (112)	0.15517 (39)	0.40298 (99)	465 (73)
C24	0.44095 (99)	0.19880 (31)	0.19680 (88)	335 (59)
C25	0.53286 (126)	0.20913 (35)	0.11575 (104)	472 (76)
C26	0.55961 (149)	0.25235 (42)	0.09220 (125)	619 (96)
C27	0.49905 (145)	0.28321 (41)	0.15016 (132)	626 (96)
C28	0.41211 (131)	0.27395 (36)	0.23393 (137)	595 (91)
C29	0.38131 (117)	0.23173 (36)	0.25767 (110)	486 (76)
C30	-0.00405 (118)	0.20519 (36)	-0.07656 (94)	445 (71)

$${}^a U_{\text{eq}} = [1/(6\pi^2)] \sum \sum \beta_{ij} a_i a_j$$

Table IV. Selected Bond Lengths in 3 (Å)

Re–P1	2.414 (2)	C4–C5	1.507 (13)
Re–P2	2.311 (3)	C5–C30	1.528 (13)
Re–N	1.788 (8)	Cl3–C30	1.788 (10)
N–O	1.197 (10)	Cl4–C30	1.796 (12)
Re–C1	2.272 (10)	Cl5–C30	1.764 (11)
Re–C2	2.207 (10)	P2–C11	2.043 (4)
Re–C3	2.206 (10)	P2–Cl2	2.105 (4)
Re–C4	2.265 (10)	P2–C6	1.814 (9)
C1–C2	1.432 (13)	P1–C24	1.827 (10)
C1–C5	1.530 (13)	P1–C18	1.837 (9)
C2–C3	1.357 (17)	P1–C12	1.857 (9)
C3–C4	1.468 (16)		

(phosphine) complex derived by (1) CCl₃ addition to the cyclopentadienyl ligand of 2 and (2) chlorine atom addition to the chlorophosphido ligand of 2.

5. Other Reactions of Functionalized Phosphido Complexes.

The chlorophenylphosphido complex 2 was generated in situ at

Table V. Selected Bond Angles in 3 (deg)

P2-Re-P1	99.32 (9)	Re-P2-Cl2	123.6 (1)
N-Re-P1	101.4 (3)	C6-P2-Cl1	101.0 (3)
N-Re-P2	96.2 (3)	C6-P2-Cl2	97.3 (3)
Re-N-O	176.5 (8)	C11-P2-Cl2	98.2 (2)
C1-C2-C3	108.4 (9)	P2-C6-C7	117.3 (7)
C2-C3-C4	107.3 (9)	P2-C6-C11	122.7 (7)
C3-C4-C5	107.8 (9)	Re-P1-Cl2	112.4 (3)
C4-C5-C1	95.3 (8)	Re-P1-Cl8	114.9 (3)
C5-C1-C2	108.2 (8)	Re-P1-C24	118.0 (3)
C4-C5-C30	115.5 (8)	C12-P1-C18	104.1 (4)
C1-C5-C30	116.0 (9)	C12-P1-C24	103.8 (5)
C5-C30-C15	116.1 (8)	C18-P1-C24	102.1 (4)
C5-C30-C13	109.0 (7)	P1-C12-C13	120.5 (8)
C5-C30-C14	107.6 (7)	P1-C12-C17	119.9 (7)
C15-C30-C13	107.3 (6)	P1-C18-C19	121.9 (7)
C15-C30-C14	109.0 (6)	P1-C18-C23	120.0 (7)
Cl3-C30-C14	107.6 (6)	P1-C24-C25	122.9 (8)
Re-P2-C6	119.5 (3)	P1-C24-C29	117.8 (7)
Re-P2-Cl1	113.1 (1)		

-98 °C and treated with a variety of potential chloride-abstracting reagents (AlCl_3 , SnCl_4 , $\text{CF}_3\text{SO}_2\text{SiMe}_3$, $\text{Ph}_3\text{C}^+\text{PF}_6^-$). Analysis by $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P NMR spectroscopy indicated the formation of extensive mixtures of products. None of these exhibited lower field resonances than **2** or were otherwise suggestive of a phosphinidene complex.

Low-temperature reactions of the *tert*-butylchlorophosphido complex **9** with AlCl_3 and $\text{CF}_3\text{SO}_2\text{SiMe}_3$ similarly gave a multitude of products. However, reaction of **9** and $\text{Ph}_3\text{C}^+\text{PF}_6^-$ proceeded cleanly at -91 °C. An intermediate formed, which converted above -30 °C to a product that was subsequently isolated in low yield as a yellow powder. The ^1H and ^{13}C NMR spectra of this material (Experimental Section) indicated that Ph_3C had been incorporated. The presence of vinyl proton and carbon resonances suggested the disruption of one aromatic ring. Although the further characterization of this probable bis(phosphine) complex was not pursued, attack of phosphorus nucleophiles upon a para carbon of Ph_3C^+ has precedence.¹⁸ No low-field ^{31}P NMR resonances were noted during the course of this reaction.

Di(phenoxy)phosphido complex **10** and $\text{Ph}_3\text{C}^+\text{PF}_6^-$ also cleanly reacted, as assayed by ^{31}P NMR spectroscopy, to give a product that persisted up to room temperature. However, isolation attempts were unsuccessful. Complex **10** also reacted less cleanly with AlCl_3 and $\text{CF}_3\text{SO}_2\text{SiMe}_3$ to give thermally unstable products.

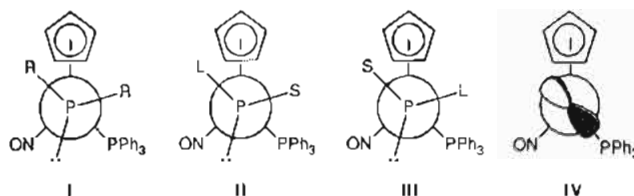
Discussion

1. Synthesis and Properties of Functionalized Phosphido Complexes. There have been a variety of approaches to the synthesis of functionalized phosphido complexes, several of which are particularly relevant to those in Schemes I-III. For example, Roper has reported the reaction of the osmium phenylphosphido complex $\text{Os}(\text{CO})_2(\text{PPh}_3)_2(\text{Cl})(\text{PPhH})$ and I_2 to give tris(phosphine) complex $[\text{Os}(\text{CO})_2(\text{PPh}_3)_2(\text{Cl})(\text{PPhH})]^+\text{I}^-$, with subsequent deprotonation to the iodophenylphosphido complex $\text{Os}(\text{CO})_2(\text{PPh}_3)_2(\text{Cl})(\text{PPhI})$.^{7c} This provides an alternative to our method for the replacement of phosphido ligand phosphorus-hydrogen bonds by phosphorus-halogen bonds (Scheme I). We are not aware of other direct, single-step protocols. Also, Malisch has previously reported the reaction of iron and ruthenium anions $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2]^-$ and *t*-BuPCl₂ to give *tert*-butylchlorophosphido complexes $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2(\text{P}(t\text{-Bu})\text{Cl})$.^{7a,b} We analogously prepare the *tert*-butylchlorophosphido complex **9** from rhenium anion **8** (Scheme III). However, we are not aware of previous reports of the displacement of phenoxy groups from $\text{P}(\text{OPh})_3$ by transition-metal anions, as in the conversion of **8** to **10**.

The low thermal stabilities of the functionalized rhenium phosphido complexes hampered their evaluation as precursors to the target phosphinidene complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(=\text{PX})]^+\text{X}^-$. However, an increasing body of data suggests that

cationic phosphinidene complexes are extremely electrophilic at phosphorus, affording facile intra- and intermolecular decomposition pathways.^{1,4,19} The only isolable phosphinidene complexes, $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}=\text{PAr}$ ($\text{M} = \text{Mo}, \text{W}$; $\text{Ar} = 2,4,6\text{-C}_6\text{H}_2(t\text{-Bu})_3$), are neutral and sterically shielded at phosphorus.⁵ We had hoped to determine the rate law for a substitution reaction such as the conversion of **2** to **5** (Scheme II). For example, a zero-order dependence upon $\text{P}(\text{NMe}_2)_3$ concentration would suggest an intermediate phosphinidene complex. However, we have not yet found a transformation that is spectroscopically clean and involves a precursor that can be isolated in pure form.

We have previously shown that symmetrically substituted, dialkyl- and diarylphosphido complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{PR}_2)$ preferentially adopt $\text{Re}-\text{PR}_2$ conformations of type I and that the diastereotopic phosphido substituents are easily



exchanged ($\Delta G^\ddagger = 12.6\text{--}14.9$ kcal/mol).² Exchange requires both phosphorus inversion and $\text{Re}-\text{PR}_2$ bond rotation. Unsymmetrically substituted, functionalized phosphido complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{PXX}')$ would be expected to adopt analogous $\text{Re}-\text{PXX}'$ conformations, as represented by the diastereomeric structures II and III. Phosphorus inversion and $\text{Re}-\text{PXX}'$ bond rotation now interconvert diastereomers. Since diastereomers of chlorophosphido complexes **2** and **9** equilibrate below room temperature, phosphorus inversion barriers must be low. However, electronegative (and π -donor) substituents raise phosphorus inversion barriers,²⁰ and **9** shows no sign of the low-temperature NMR coalescence behavior that is routinely observed with alkyl- and aryl-substituted complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{PR}_2)$.² The ^{13}C NMR data for the diastereotopic phenoxy groups of symmetrically substituted **10** (Table I) indicate a barrier of at least 14.9 kcal/mol (ΔG^\ddagger , 308 K) for their exchange.

We have previously shown that diastereomers of type II are more stable than those of type III for alkyl complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CHLS})$, where L and S are large and small C_α substituents.²¹ The region between the small nitrosyl and medium-sized cyclopentadienyl ligands can best accommodate the largest substituent. Conversely, the region between the nitrosyl and PPh_3 ligands is most crowded.²² However, the equilibrium diastereomer ratios for chlorophosphido complexes **2** and **9** appear to be ca. 50:50. This is especially surprising in view of the large size difference of the *tert*-butyl and chloro substituents in **9**. However, there may be a compensating electronic preference for the chloride substituent to be oriented anti to the PPh_3 ligand as in III. This would allow overlap of the rhenium fragment HOMO, which is the d orbital depicted in IV,^{2,23} with the vacant $\text{P}-\text{Cl}$ σ^* orbital. Such an interaction is, in valence-bond terms, equivalent to a phosphinidene-complex resonance contributor. Polar bonds have been shown to alter rotameric equilibria from that expected from steric considerations in related iron complexes.²⁴ Interestingly, one of the diastereomers of **9** exhibits a $^2J_{\text{PP}}$ that is much greater (63.3 Hz in THF, 65.6 Hz in C_6D_6) than those of the other functionalized phosphido complexes (21-32 Hz), or the dialkyl- and diarylphosphido complexes reported previously (13-15 Hz).²

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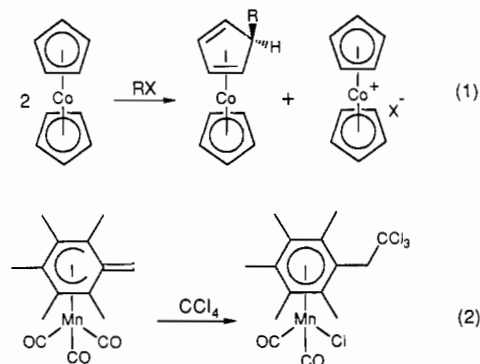
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Scheme V. Related Additions of Alkyl Halides to Ligands in Organometallic Complexes

This indicates a considerable perturbation of the usual $\text{Ph}_3\text{P-Re-PXX}'$ geometry and/or orbital interactions.

The $\text{PPh-P}(\text{NMe}_2)_3$ complex **5**, in which the electronegative phosphido substituent is also the sterically most demanding, appears to exist as one diastereomer. Schultz and Parry have previously described the characterization of diphosphorus cations such as $[(\text{Me}_2\text{N})_2\text{P-P}(\text{NMe}_2)_3]^+\text{AlCl}_4^-$.²⁵ To our knowledge, **5** is the first transition-metal analogue to diphosphorus cations of this type. Complex **5** can also be considered a metal complex of the closed-shell species $\text{PhP}=\text{P}(\text{NMe}_2)_3$. Such phosphinidene phosphoranes are rare and unstable; only a few examples, such as $\text{F}_3\text{CP}=\text{PMe}_3$, have been studied.^{12a,26}

2. Synthesis and Properties of the η^4 -Cyclopentadiene Complex

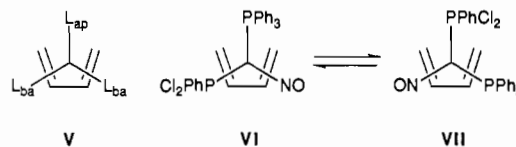
3. Complex **3** is formally derived from a 1,3-addition of CCl_4 to the phosphido complex **2** (Scheme IV). Note also that two different ligands, as opposed to the metal and a ligand, serve as the addition termini. Although we are unaware of close precedents for this reaction, related 1,*n*-additions to electron-rich organometallic compounds have been observed. For example, a number of organic halides, including CCl_4 , have been found to undergo binuclear addition to cobaltocene as shown in eq 1 of Scheme V.²⁷ Eyman has recently reported the 1,4-addition of CCl_4 to a manganese cyclohexadienyl complex, as shown in eq 2 of Scheme V.²⁸

The cobaltocene additions in Scheme V have usually been interpreted as nonchain radical reactions involving initial charge transfer from cobalt to the alkyl halide.^{27c} Since the formation of **3** is dramatically inhibited in the presence of the radical trap duroquinone, a chain process likely operates in Scheme IV. Transient colors are generated upon addition of CCl_4 to **1** or **2** at -98°C , suggesting initial charge transfer. Charge-transfer complexes of iron group metallocenes and a variety of chlorocarbons have been characterized.²⁹ It has also been shown that radical chain reactions of CCl_4 and organomercurials can be initiated by charge transfer.³⁰ However, it is well-known that PPh_3 and CCl_4 react to give the ion pair $\text{Ph}_3\text{PCl}^+\text{CCl}_3^-$,³¹ and thus a heterolytic pathway to **3** is in principle possible.

Although the conversion of **2** to **3** constitutes an overall oxidation, the rhenium center is actually reduced from a +1 (d^6) to a -1 (d^8) oxidation state. Hence, **3** is isoelectronic with an extensively studied class of compounds, (η^4 -1,3-diene) FeL_3 com-

plexes.³² The only other structurally characterized rhenium η^4 -1,3-cyclo-diene complex that we are aware of, (η^4 - C_5H_6) $\text{Re}(\text{PPh}_3)_2\text{H}_3$,³³ differs considerably in coordination number and oxidation state. The crystal structure of a cobalt η^4 - $\text{C}_5\text{H}_5\text{CCl}_3$ complex has been very recently determined.³⁴

Numerous structural studies have established that (η^4 -1,3-diene) FeL_3 complexes adopt square-pyramidal structures of the type shown in the idealized projection V, with (1) the 1,3-diene ligands



in basal (ba) positions, and (2) the C1-C4 diene termini syn to the apical (ap) ligand.³² Furthermore, the best π -accepting non-diene ligands preferentially occupy the basal positions.^{32b} For (η^4 -1,3-diene) $\text{Fe}(\text{CO})_3$ complexes, $\text{CO}_{\text{ap}}-\text{Fe}-\text{CO}_{\text{ba}}$ bond angles range from 95 to 103° (mean 100°), and $\text{CO}_{\text{ba}}-\text{Fe}-\text{CO}_{\text{ba}}$ bond angles range from 89 to 94° (mean 92°).^{30a} Accordingly, we assign the PPh_3 ligand in the solid-state structure of **3** (Figure 2) to an apical position based upon (1) its geometrical relationship to the C1-C4 termini of the diene moiety, (2) the resulting placement of the good π -accepting nitrosyl ligand in a basal position, and (3) the fact that the $\text{Ph}_3\text{P-Re-PPhCl}_2$ and $\text{Ph}_3\text{P-Re-NO}$ bond angles ($L_{\text{ap}}-\text{Re}-L_{\text{ba}} = 99.32$ (9°) and 101.4 (3°)) are larger than the ON-Re-PPhCl_2 bond angle ($L_{\text{ba}}-\text{Re}-L_{\text{ba}} = 96.2$ (3°)). An idealized representation of the solid-state structure of **3** is given in VI.

Complexes of the formula (η^4 -1,3-diene) FeL_3 often exhibit fluxional NMR behavior resulting from the exchange of the L_3 ligands between the basal and apical positions. Hence, the decoupling observed in low-temperature NMR spectra of **3** (Figure 1 and text) is likely due to a slowing of the interconversion of diastereomeric structures VI and VII. Isomer VII retains the nitrosyl ligand in a basal position, in contrast to a third possible isomer that is not depicted. Isomers VI and VII are chiral, and it is possible that VI might convert directly to the mirror image of VII (through exchange of just the two phosphine ligands). However, studies with iron complexes show a cyclical exchange of all three non-diene ligands.^{30f}

3. Summary. Functionalized phosphido complexes (η^5 - C_5H_5) $\text{Re}(\text{NO})(\text{PPh}_3)(\text{PXX}')$ are indiscriminately reactive, as demonstrated above by transformations involving nucleophiles, electrophiles, and free radicals. This reactivity complicates their isolation and, in turn, a precise delineation of many of their physical and chemical properties. Future reports will detail our studies with the hydrogen-substituted phosphido complexes (η^5 - C_5H_5) $\text{Re}(\text{NO})(\text{PPh}_3)(\text{PHR})$,^{2b,9,35} which are much more tractable and exhibit many unusual properties.³⁶

Experimental Section

General Methods. General procedures were identical with those described previously.^{2c} Solvents were purified as follows: acetone, distilled from CaSO_4 ; CH_2Cl_2 , distilled from P_2O_5 ; benzene, ether, and THF,

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distilled from Na/benzophenone; hexane and toluene, distilled from Na; CD_2Cl_2 and C_6D_6 , vacuum transferred from CaH_2 ; THF- d_8 , vacuum transferred from LiAlH_4 .

Reagents were obtained as follows: CCl_4 (Fisher), distilled from P_2O_5 ; duroquinone (Aldrich), recrystallized from ethanol; CH_3I (Aldrich), dried over CaSO_4 , distilled, and stored over Cu; $\text{CF}_3\text{SO}_3\text{H}$ (Aldrich), distilled (760 Torr); PPhCl_2 (Strem), distilled (10^{-3} Torr); $\text{P}(\text{NMe}_2)_3$ (Aldrich), distilled (15 Torr) from CaH_2 ; SnCl_4 (Aldrich), used as received; AlCl_3 (MCB), sublimed (10^{-3} Torr, 120 °C) from Al/NaCl powder; $\text{Ph}_3\text{C}^+\text{PF}_6^-$ (Columbia Organics or Aldrich), precipitated from $\text{CH}_2\text{Cl}_2/\text{benzene}$ or $\text{CH}_2\text{Cl}_2/\text{ethyl acetate}$; $\text{CF}_3\text{SO}_3\text{SiMe}_3$ (Petrarch), distilled from CaH_2 ; $n\text{-BuLi}$ (Alfa, 2.5 M in hexane), standardized by a literature procedure;³⁷ $t\text{-BuPcCl}_2$ (Strem), used as received. $\text{P}(\text{O}i\text{Pr})_3$ (Eastman) was dissolved in ether and washed with 5% aqueous NaOH , H_2O , and saturated aqueous NaCl and the ether solution then dried over Na_2SO_4 and distilled (10^{-3} Torr).

Preparation of $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{PPhCl})$ (2). A 5-mm NMR tube was charged with $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{PPhH})$ (1; 0.030 g, 0.046 mmol)^{2b,9} and THF (0.400 mL), and was capped with a septum and cooled to -98 °C (MeOH/N_2 bath). Then CCl_4 (4.9 μL , 0.008 g, 0.05 mmol) was added by syringe and the sample was placed in a -90 °C NMR probe. A $^{31}\text{P}\{\text{H}\}$ NMR spectrum showed an 80:20 mixture of diastereomers **2a** and **2b** (Table I), and other features noted in the results section.

An identical experiment was conducted in which CCl_4 addition was immediately followed by injection of a solution of duroquinone (0.023 g, 0.138 mmol) in THF (0.100 mL). For data see the Results section. Comparable experiments in CH_2Cl_2 and THF- d_8 are fully described elsewhere.⁹

Preparation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{PPhMeCl})]^+\text{I}^-$ (4). A Schlenk tube was charged with **1** (0.200 g, 0.306 mmol), THF (3 mL), and a stir bar. The solution was cooled to -98 °C with stirring, and CCl_4 (32 μL , 0.051 g, 0.33 mmol) was added dropwise by syringe. The mixture was kept at -98 °C for 20 min to ensure complete generation of **2**. Then MeI (48 μL , 0.11 g, 0.77 mmol) was added dropwise by syringe and the vessel was transferred to a -78 °C bath. After 10 min, the bath was removed and the tube was allowed to warm (ca. 10 min). Solvent was removed in vacuo, and the resulting yellow oil was extracted with 6:1 (v/v) THF/ CH_2Cl_2 (4 mL). The extract was filtered and stored at -25 °C for 1 day. A yellow precipitate formed and was collected by filtration, washed with THF, and dried in vacuo (56 °C) to give **4** (0.167 THF as a $(47 \pm 2): (53 \pm 2)$ mixture of diastereomers (0.163 g, 0.194 mmol, 63%), mp 216–217 °C dec. Anal. Calcd for $\text{C}_{30}\text{H}_{28}\text{ClINOP}_2\text{Re}\cdot 0.167\text{C}_4\text{H}_8\text{O}$: C, 43.79; H, 3.52; Cl, 4.22; I, 15.09. Found: C, 43.75; H, 3.76; Cl, 4.71; I, 15.15. The degree of THF solvation ($1/6$) was reproducible. Recrystallization of **4** from $\text{CH}_2\text{Cl}_2/\text{ether}$ gave unsolvated gold-colored nuggets that were dried in vacuo (56 °C); mp 190–201 °C dec. A ^1H NMR spectrum showed a *third* isomer (Results section). Anal. Calcd for $\text{C}_{30}\text{H}_{28}\text{ClINOP}_2\text{Re}$: C, 43.46; H, 3.40. Found: C, 43.27; H, 3.49.

Preparation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{PPhCl}_2)]^+\text{CF}_3\text{SO}_3^-$ (7). A Schlenk flask was charged with $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_3)$ (1.50 g, 2.69 mmol),³⁸ CH_2Cl_2 (50 mL), and a stir bar. The solution was cooled to -23 °C with stirring, and $\text{CF}_3\text{SO}_3\text{H}$ (301 μL , 0.402 g, 2.69 mmol) was added. The cooling bath was removed, and the flask was allowed to warm to room temperature (ca. 10 min) to generate $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{OSO}_2\text{CF}_3)$.¹² Then PPhCl_2 (732 μL , 0.960 g, 5.38 mmol) was added. After 2 days the solvent was removed in vacuo. The resulting yellow solid was recrystallized from $\text{CH}_2\text{Cl}_2/\text{ether}$ to give air-stable yellow needles of **7** that were collected by filtration, washed with ether, and dried in vacuo (56 °C) (1.87 g, 2.14 mmol, 80%), mp 211–216 °C dec. Anal. Calcd for $\text{C}_{30}\text{H}_{25}\text{F}_3\text{NO}_4\text{ReSCl}_2$: C, 41.34; H, 2.89. Found: C, 41.16; H, 2.83.

Preparation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{PPh}(\text{NMe}_2)_3)]^+\text{Cl}^-$ (5). **Method A.** Complex **2** was generated from **1** (0.035 g, 0.054 mmol) and CCl_4 (5.4 μL , 0.009 g, 0.059 mmol) in THF- d_8 at -98 °C as described above. After 10 min, the NMR tube was transferred to a -78 °C bath, and $\text{P}(\text{NMe}_2)_3$ (29 μL , 0.026 g, 0.16 mmol) was added by syringe. The tube was then kept in a -41 °C bath for 4 h. Finally, the tube was stored at -25 °C for 20 h. The sample was analyzed at -15 °C by ^1H , $^{13}\text{C}\{\text{H}\}$, and ^{31}P NMR spectroscopy. These data, which were very close to those obtained below, are compiled in ref 9 and indicated a 55% yield of **5**.

Method B. A 5-mm NMR tube was charged with **7** (0.034 g, 0.039 mmol) and CD_2Cl_2 (0.400 mL) and was capped with a septum. The tube was cooled to -78 °C and $\text{P}(\text{NMe}_2)_3$ (15 μL , 0.013 g, 0.083 mmol) was

added by syringe. The sample was stored at -25 °C for 12 h and then analyzed by ^1H , $^{13}\text{C}\{\text{H}\}$, and $^{31}\text{P}\{\text{H}\}$ NMR. Data on **5** (ca. 70%): Table I. Data on $[(\text{Me}_2\text{N})_3\text{PCl}]^+\text{X}^-$ (CD_2Cl_2): ^1H NMR δ 2.93 (d, $J_{\text{HP}} = 12.7$ Hz); $^{31}\text{P}\{\text{H}\}$ NMR 53.48 ppm (s). Lit. data on $[(\text{Me}_2\text{N})_3\text{PCl}]^+\text{Cl}^-$ (CDCl_3):¹⁴ ^1H NMR δ 3.10 (d, $J_{\text{HP}} = 12.0$ Hz); $^{31}\text{P}\{\text{H}\}$ NMR 50.8 ppm (s). Data on an unidentified minor (ca. 20%) product (CD_2Cl_2): ^1H NMR δ 5.48 (s, C_5H_5); $^{31}\text{P}\{\text{H}\}$ NMR (ppm) 112.32 (d, $J_{\text{PP}} = 12.8$ Hz), 8.04 (d, $J_{\text{PP}} = 12.8$ Hz).

Preparation of $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{P}(t\text{-Bu})\text{Cl})$ (9). **Method A.** A 5-mm NMR tube was charged with $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H})$ (0.016 g, 0.029 mmol)¹⁵ and THF (0.250 mL) and was capped with a septum. The tube was placed in a -15 °C bath, and $n\text{-BuLi}$ (15 μL , 0.37 mmol; 2.49 M in hexane) was added by syringe. After 15 min to allow the complete generation of $\text{Li}^+[(\eta\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)]^-$,¹⁵ the tube was transferred to a -78 °C bath and a solution of $t\text{-BuPcCl}_2$ (0.023 g, 0.15 mmol) in THF (0.150 mL) was added by syringe. The resulting light orange solution was analyzed by $^{31}\text{P}\{\text{H}\}$ NMR. Spectral data: Results section.

Method B. This experiment was performed under subdued lighting. A Schlenk tube was thoroughly flame-dried in vacuo and charged with $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H})$ (0.500 g, 0.919 mmol), THF (10 mL), and a stir bar. The solution was stirred and placed in a -15 °C bath. Then $n\text{-BuLi}$ (456 μL , 1.10 mmol; 2.41 M in hexane) was added by syringe. After 15 min, the tube was placed in a -98 °C bath. A solution of $t\text{-BuPcCl}_2$ (0.292 g, 1.84 mmol) in THF (5 mL) was slowly added by syringe along the wall of the vessel, so as to be chilled prior to entering the reaction mixture. The red solution lightened, and after 15 min the cold bath was removed. Solvent was evaporated in vacuo as the mixture warmed. The resulting dull orange solid was extracted with benzene (30 mL). The extract was filtered, and solvent was removed from the filtrate in vacuo. The resulting solid was triturated with hexane (17 mL), collected by filtration, washed with hexane (8 mL), and dried in vacuo (56 °C). This gave crude **9** as an air-sensitive dull red powder (0.440 g, 0.660 mmol, 72%), mp 186–188 °C dec. Spectral analysis (Table I) showed **9** to be of $\geq 90\%$ purity. Mass spectrum (EI, m/e , $^{187}\text{Re}^{35}\text{Cl}$, 17 eV): 667 (M^+ , 1%), 610 ($\text{M}^+ - \text{C}_4\text{H}_9$, 1%), 579 ($\text{M}^+ - \text{PC}_6\text{H}_5$, 12%), 262 (PPh_3^+ , 100%), 108 (PPh^+ , 9%). Further purification attempts are detailed in ref 9.

Preparation of $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{P}(\text{OPh})_2)$ (10). The hydride complex $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H})$ (0.500 g, 0.919 mmol) and $n\text{-BuLi}$ (494 μL , 1.19 mmol; 2.41 M in hexane) were combined as described in preparation B of **9**. The Schlenk tube was transferred to a -78 °C bath, and $\text{P}(\text{OPh})_3$ (1.21 mL, 1.43 g, 4.60 mmol) was added by syringe. The red solution rapidly turned orange. After 2 h, the cold bath was removed and solvent was evaporated in vacuo at ambient temperature. The resulting orange oil was washed with hexane (2×20 mL) and then extracted into ether (ca. 15 mL). The extract was filtered and cooled to -78 °C. A solid precipitated, which was collected by filtration and washed with ether. A small second crop precipitated from the hexane washes. The combined crops were dried in vacuo to afford crude **10** as an air-sensitive orange powder (0.400 g, 0.526 mmol, 57%). Analysis by ^1H and $^{31}\text{P}\{\text{H}\}$ NMR indicated ca. 95% purity. Samples of **10** bleached over the course of a few days under fluorescent lighting, and hence were recrystallized from benzene/hexane in the dark. This gave orange crystals of **10** ($0.5\text{C}_6\text{H}_{14}$, which were collected by filtration, rinsed with hexane, and dried in vacuo (25 °C, 3 days); mp 193–198 °C dec. Anal. Calcd for $\text{C}_{33}\text{H}_{30}\text{NO}_3\text{P}_2\text{Re}\cdot 0.5\text{C}_6\text{H}_{14}$: C, 56.78; H, 4.63. Found (analysis on two separate samples): C, 56.52, 56.23; H, 4.52, 4.56. Mass spectrum (EI, m/e , ^{187}Re , 17 eV): 761 (M^+ , 3%), 684 ($\text{M}^+ - \text{C}_6\text{H}_5$, 2%), 668 ($\text{M}^+ - \text{C}_6\text{H}_5\text{O}$, 10%), 262 (PPh_3^+ , 100%), 94 ($\text{C}_6\text{H}_5\text{OH}^+$, 32%).

Preparation of $(\eta^4\text{-C}_5\text{H}_5\text{CCl}_3)\text{Re}(\text{NO})(\text{PPh}_3)(\text{PPhCl}_2)$ (3). A Schlenk tube was charged with **1** (0.250 g, 0.383 mmol), THF (4.5 mL), and a stir bar. The tube was cooled to -78 °C with stirring, and CCl_4 (74 μL , 0.118 mg, 0.767 mmol) was added dropwise by syringe. After 3 h the cold bath was removed, and the solvent was evaporated in vacuo as the mixture warmed. The resulting yellow residue was extracted with benzene (4 mL). The extract was filtered and layered with hexane. A precipitate formed (0 °C, 12 h) that was collected by filtration, washed with acetone (3×1 mL), and dried in vacuo (78 °C) to afford **3** (0.167 C_6H_6 as an air-stable orange powder (0.211 g, 0.247 mmol, 65%), mp 151–161 °C dec. Anal. Calcd for $\text{C}_{30}\text{H}_{25}\text{Cl}_3\text{NOP}_2\text{Re}\cdot 0.167\text{C}_6\text{H}_6$: C, 43.60; H, 3.07; Cl, 20.76. Found: C, 43.73, 43.71; H, 3.09, 2.84; Cl, 19.93, 20.36. The degree of solvation ($1/6$) was determined by ^1H NMR integration and was reproduced in separate preparations. Mass spectrum (EI, m/e , ^{187}Re , 17 eV): 579 ($[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(^{35}\text{Cl})]^+$, 49%), 262 (PPh_3^+ , 62%), 180 ($(\text{PPh}^{37}\text{Cl}^{35}\text{Cl})^+$, 100%), 143 ($(\text{PPh}^{35}\text{Cl})^+$, 33%), 117 ($\text{C}^{35}\text{Cl}_3^+$, 19%), 108 (PPh^+ , 21%). Mass spectrum (positive Ar FAB, glycerol/15-crown-5 matrix, m/e , ^{187}Re , 6–8 KeV) 872 (10%), 842 (8%), 806 (8%), 722 (42%), 686 (75%), 668 (40%), 544 (100%; data normalized to this peak).

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Samples of 3·0.167C₆H₆ were dissolved in CH₂Cl₂ and kept at -25 °C for several days. Orange irregular crystals of unsolvated **3** precipitated, which were collected by filtration and dried in vacuo (78 °C); mp 152-171 °C dec. Anal. Calcd for C₃₀H₂₃Cl₃NOP₂Re: C, 42.85; H, 3.00; Cl, 21.08. Found: C, 43.06, 42.89; H, 3.13, 3.05; Cl, 20.63, 21.47.

Crystal Structure of 3. Unit cell determination and data collection were performed on a Syntex P1 diffractometer as outlined in Table II (see also supplementary material). The unit cell was determined using 15 centered reflections with 16° < 2θ < 29°. A structure was solved with standard heavy-atom techniques, using the UCLA crystallographic package.³⁹ Empirical absorption corrections were made, and hydrogen atoms were placed in calculated positions. Non-hydrogen atoms were refined with anisotropic thermal parameters. No extinction corrections were made.

Reactions of 2, 9, and 10 with Potential Halide-Abstracting Reagents and Related Compounds. Full details of these experiments are described elsewhere.⁹ Representative reactions are as follows.

Experiment A. A 5-mm NMR tube was charged with **9** (0.030 g, 0.045 mmol) and Ph₃C⁺PF₆⁻ (0.018 g, 0.046 mmol) and was capped with a septum, connected to a vacuum line, and evacuated. The tube was cooled to -196 °C and CH₂Cl₂ (0.400 mL) was added. The mixture was freeze-thaw (ca. -90 °C) degassed and placed under N₂. The sample was transferred to a -91 °C NMR probe. ³¹P{¹H} NMR: 126.65 (br s), 107.04 (br s), 7.78 ppm (d, J_{PP} = 14.0 Hz); no ¹J_{PH} coupling was observed in the ¹H-coupled spectrum. The 126.65 and 107.04 resonances showed reversible coalescence (T_c ca. -60 °C) to a broad singlet at 118.38 ppm (-30 °C); the 7.78 ppm resonance did not exhibit temperature dependence (-91 to -30 °C). The sample was kept at room temperature for 10 min and then returned to the -30 °C NMR probe. The ³¹P{¹H} NMR spectrum showed the disappearance of the resonances noted above and a new major product [132.57 (d, J_{PP} = 23.0 Hz), 10.87 ppm (d, J_{PP} = 23.0 Hz)] and minor product resonances; no ¹J_{PH} coupling was observed in the ¹H-coupled spectrum.

Experiment B. A Schlenk tube was charged with **9** (0.283 g, 0.424 mmol), Ph₃C⁺PF₆⁻ (0.165 g, 0.425 mmol), and a stir bar and was cooled to -78 °C. Then THF (5 mL) was added by syringe, and the mixture was stirred. The resulting red slurry was transferred to a -23 °C bath. Within 30 min a yellow precipitate formed. The cold bath was removed, and when the mixture reached room temperature, the solid was collected

by filtration, washed with THF (1 mL), washed with hexane (2 × 5 mL), and dried in vacuo (56 °C). This gave a yellow solid in low yield (0.047 g); mp 155-161 °C dec. Data: IR (cm⁻¹, KBr) 3125-2868 w, ν_{NO} 1710 vs, 1483 m, 1464 m, 1436 m, 1420 m, 1400 w, 1369 w, 1162 w, 1151 w, 1090 m, 1063 m, 1027 w, 1014 w, 1000 w, ν_{PF} 840 vs vbr, 773 m, 746 m, 699 s, 649 w, 632 w, 624 w; ³¹P{¹H} NMR (ppm, CD₂Cl₂, -41 °C) 132.36 (d, J_{PP} = 23.0 Hz), 10.95 (d, J_{PP} = 23.0 Hz); ¹H NMR (δ, CD₂Cl₂, -15 °C) 7.58-7.33 (m, 20 H), 7.13-7.09 (m, 5 H), 6.83-6.76 (m, 1 H), 6.33-6.26 (m, 1 H), 6.02-5.93 (m, 1 H), 5.75 (s, 5 H, C₅H₅), 5.01 (br d, J_{HP} = ca. 36 Hz, 1 H), 4.90-4.82 (m, 1 H), 3.71-3.67 (m, 1.0 × 4 H, THF solvate), 1.85-1.80 (m, 1.0 × 4 H, THF solvate), 1.52 (d, J_{HP} = 17.7 Hz, 9 H, *t*-Bu); ¹³C{¹H} NMR (ppm, CD₂Cl₂, -15 °C) phenyl/vinyl carbons and 92.28 (s, C₅H₅), 68.15 (s, THF), 48.17 (d, J_{CP} = 20.7 Hz, CMe₃), 28.08 (br s, CH₃).

Experiment C. A 5-mm NMR tube was charged with **10** (0.065 g, 0.086 mmol) and CH₂Cl₂ (0.100 mL) and was capped with a septum, connected to a vacuum line, cooled to -196 °C, and evacuated. Then a solution of Ph₃C⁺PF₆⁻ (0.037 g, 0.095 mmol) in CH₂Cl₂ (0.300 mL) was added by syringe and the mixture was freeze-thaw (ca. -90 °C) degassed and placed under N₂. The sample was transferred to a -90 °C NMR probe and gradually warmed. The ³¹P{¹H} NMR spectrum showed a product that persisted up to room temperature. No decomposition was observed after 10 min at room temperature, but attempted recrystallization from CH₂Cl₂/ether was unsuccessful. Spectral data: ³¹P{¹H} NMR (ppm, CH₂Cl₂, -30 °C) 133.58 (d, J_{PP} = 21.8 Hz), 11.29 (d, J_{PP} = 21.8 Hz); no ¹J_{PH} coupling was observed in the ¹H-coupled spectrum.

Experiment D. A 5-mm NMR tube was charged with **10** (0.35 g, 0.046 mmol) and AlCl₃ (0.012 g, 0.092 mmol) and was capped with a septum, connected to a vacuum line, and evacuated. The tube was cooled to -196 °C, and CH₂Cl₂ (0.400 mL) was added. The mixture was freeze-thaw (ca. -90 °C) degassed and placed under N₂. The sample was transferred to a -90 °C NMR probe. ³¹P{¹H} NMR (ppm, -90 °C): 143.2 (br s), 13.2 (br s), and minor resonances. The 143 ppm resonance showed ¹J_{PH} = 489 Hz in a ¹H-coupled spectrum. Extensive deterioration of the sample began upon warming to -50 °C.

Acknowledgment. We thank the NSF for support of this research, Professor G. Bertrand (Université Paul Sabatier) for valuable discussions, Professor D. P. Eyman (University of Iowa) for a preprint of ref 28, Professor J. M. O'Connor (University of California, San Diego) for a preprint of ref 34, and B. D. Zwick and M. A. Dewey for technical assistance.

Supplementary Material Available: Full versions of Tables II, IV, and V and a table of anisotropic thermal parameters (4 pages); a table of calculated and observed structure factors for **3** (22 pages). Ordering information is given on any current masthead page.

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The Reaction of Cobaltocene with Secondary Phosphine Oxides Revisited. Trapping of an Intermediate Cobalt(I) Complex

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Received January 27, 1989

The secondary phosphine oxides HP(O)R₂ (R = *n*-butyl (**1a**), isobutyl (**1b**), cyclohexyl (**1c**) and 9*H*-9-phosphabicyclononane 9-oxide (**1d**)) have been prepared. They react at room temperature with bis(cyclopentadienyl)cobalt to yield dihydrogen and cobalt(I) compounds of the type [(C₅H₅)Co(1-*exo*-R'-C₂H₅)] (R' = P(O)R₂ (**2a-d**)). The complexes **2a,b** have also been prepared from cobaltocenium iodide and in situ prepared solutions of KP(O)(*n*-butyl)₂ and KP(O)(isobutyl)₂, respectively. Bis(cyclopentadienyl)cobalt, **2a**, and [(C₅H₅)Co(1-*exo*-Ph-C₂H₅)] have been shown to react with **1a,b** (but not with the more bulky phosphine oxides **1c,d**) above 100 °C to give the trinuclear cobalt(III, II) complexes [Co((C₅H₅)Co(P(O)R₂)₂)₂] (**3a,b**). **3a** is cleaved by sodium cyanide in the presence of air to yield Na[(C₅H₅)Co(P(O)R₂)₃] (**4a**) and Na₃[Co(CN)₆].

1. Introduction

The chemistry of cobaltocene (bis(cyclopentadienyl)cobalt) is dominated by its tendency to act as an electron-rich radical that can undergo one-electron-oxidation, ring-addition, and ring-substitution reactions. Secondary phosphites react with cobaltocene in a complex manner that includes both oxidation and ring substitution to produce the trinuclear complexes [Co((C₅H₅)Co(P(O)R₂)₂)₂] (R = alkoxy, **3**) in good yields. This reaction is of high synthetic value since it gives ready access to the anionic

complexes [(C₅H₅)Co(P(O)R₂)₃]⁻ (R = alkoxy, **4**), an interesting class of tris-chelating oxygen ligands. An important feature of these ligands is their rich and unusual organometallic chemistry.¹ Recently we have found that the steric as well as the electronic

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