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Synthesis of New Metallacycles of Rhenium(VII) Oxides: Migration of a Me₃Si Group To Form the *cis*-Dioxo Cyclometallaphosphoranimo Phosphane

$\overline{\text{NPPh}_2\text{CH}_2\text{PPh}_2\text{Re}(\text{O})_2(\text{OSiMe}_3)_2}$ and Arsane $\overline{\text{NPPh}_2(\text{CH}_2)_2\text{AsPh}_2\text{Re}(\text{O})_2(\text{OSiMe}_3)_2}$

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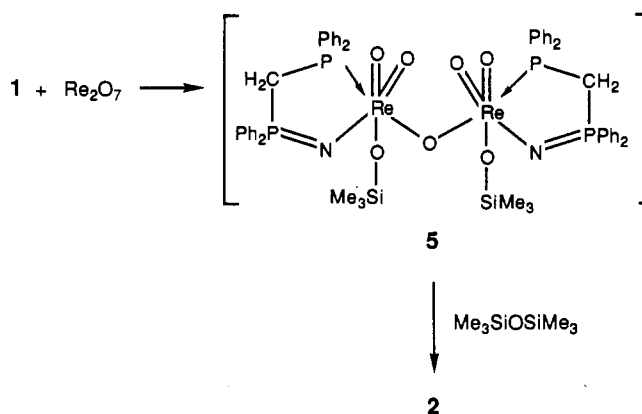
The new bifunctional phosphoranimo phosphane ligand Me₃SiN=PPh₂CH₂PPh₂ (**1**) and its arsane analogue Me₃SiN=PPh₂CH₂CH₂AsPh₂ (**3**) react with Me₃SiOREO₃ to form metallacycles $\overline{\text{NPPh}_2\text{CH}_2\text{PPh}_2\text{Re}(\text{O})_2(\text{OSiMe}_3)_2}$ (**2**) and $\overline{\text{NPPh}_2\text{CH}_2\text{CH}_2\text{AsPh}_2\text{Re}(\text{O})_2(\text{OSiMe}_3)_2}$ (**4**) in high yield via migration of a SiMe₃ group to a terminal oxygen on Re. The P(V) phosphorus atom is highly deshielded in these complexes ($\sigma(^{31}\text{P})$ 37–39 ppm), suggesting significant delocalization of electron density in the Re–N=P framework. ²⁹Si (INEPT) NMR spectroscopy shows two singlets (17.11, 7.46 ppm (**2**); 18.17, 8.25 ppm (**4**)) with no coupling to phosphorus. In each case a *cis*-dioxo structure is proposed. Reaction of **1** with Re₂O₇ gave a mixture of products, **2** and a species identified as a dimer with a ReORE bridge (**5**). Treating this mixture with (Me₃Si)₂O converted the dimer to **2**. Parallel reaction of the doubly oxidized phosphoranime Me₃SiN=PPh₂CH₂PPh₂=NSiMe₃ with Me₃SiOREO₃ gave only complex mixtures.

Introduction

High-oxidation-state rhenium, ruthenium, and osmium oxides are recognized as versatile oxidizing agents in organic synthesis.^{1,2} The toxicity of osmium tetroxide itself however suggests that it would be desirable to identify new soluble and stable high-valent oxides of rhenium and ruthenium that might fulfill equivalent roles. As a result, there is substantial interest in the chemistry of new, stable, rhenium(VII) oxo compounds. The syntheses of complexes containing a d⁰ ReO₂ fragment such as ReO₂F₃, ReO₂R₃ (R = Me, CH₂CMe₃, CH₂SiMe₃), ReO₂(CH₂CMe₃)₂Br, and ReO₂(CH₂CMe₃)₂X(py) (X = Br, Cl, F) represent significant contributions to the understanding of the structure and reactivity of this class of compounds.^{3,4}

The proven ability of phosphoranimo ligands of the type R₃P=N⁻ (which is isoelectronic with R₃P=O) to stabilize high-valent early transition metals^{5,6} suggested that we should explore the usefulness of such ligands for preparing new rhenium(VII) oxides. As part of our continuing studies on the transition-metal chemistry of new phosphorus and arsenic ligands,^{7–13} we report, herein, the synthesis and characterization of a new class

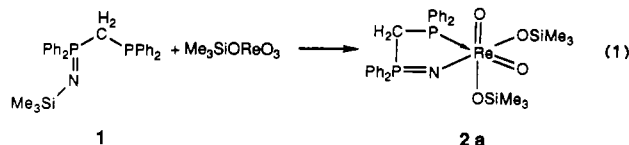
Scheme I



of stable rhenium oxo metallacycles that have been obtained via migration of –SiMe₃ groups of the new heterodifunctional ligands Me₃SiN=PPh₂CH₂PPh₂ and Me₃SiN=PPh₂(CH₂)₂AsPh₂.

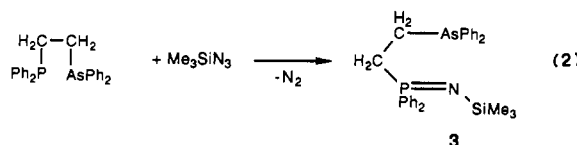
Results

The phosphoranimo phosphane Me₃SiN=PPh₂CH₂PPh₂¹¹ (**1**) reacts smoothly with trimethylsilyl perchlorate, Me₃SiOREO₃, in THF or toluene at 25 °C to produce a dark brown crystalline metallacyclic compound **2** in almost quantitative yields (eq 1).



Satisfactory analytical data and the observation of a parent ion (*m/z* 794) in the electron impact mass spectrum of **2** confirmed its chemical constitution. The monomeric compound **2** is air stable and dissolves readily in common organic solvents.

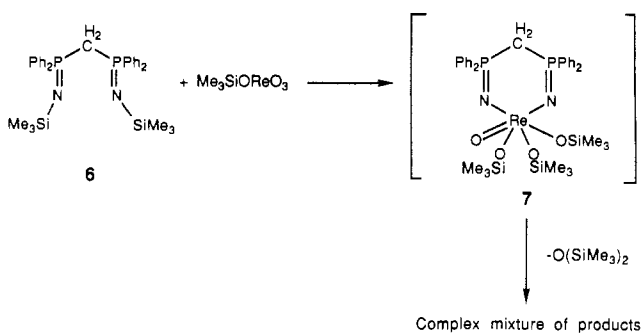
The closely related arsenic-containing ligand Me₃SiN=PPh₂(CH₂)₂AsPh₂ (**3**) was obtained from a Staudinger reaction of Me₃SiN₃ with ARPHOS (eq 2). The oxidation of ARPHOS



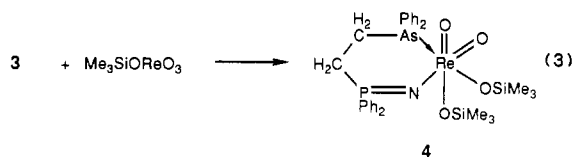
was selective at phosphorus even when the reaction was carried out in the presence of excess amounts of Me₃SiN₃.¹³ An air-stable

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Scheme II



metallacyclic compound **4** was obtained in an almost quantitative yield when **3** was allowed to react with $\text{Me}_3\text{SiOREO}_3$ in THF at 25°C (eq 3). Satisfactory analytical, mass spectrometric, and



solution molecular weight data were obtained for **4**.

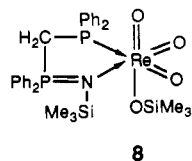
The possibility of synthesizing oxo-bridged rhenium metallacycles such as **5** (Scheme I) led us to a study of the reaction of Re_2O_7 with **1**. Suspensions of rhenium heptoxide in THF react slowly over a period of 24 h with **1**, giving solutions with a deep brown coloration. Although the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a concentrated solution from this reaction appears to be very complex, **2** is clearly identifiable as one of the products. The additional two doublets of an AX spin pattern observed in the spectrum (centered at 72.47 and 10.20 ppm; $^2J_{\text{PP}} = 23.58$ Hz) were tentatively assigned to an oxo-bridged rhenia metallacycle of the type **5**.

Attempts to separate **2** and **5** from the mixture by fractional crystallization were unsuccessful, but addition of an appropriate amount (a slight excess over the stoichiometrically required quantity) of hexamethyldisiloxane (HMDS) to this mixture of **2** and **5** resulted in an almost quantitative conversion of all of the Re species to **2** (as confirmed by the ^{31}P NMR spectrum). This transformation further supports our formulation of the intermediate oxo-bridged dimeric product **5**. The transformation sequence is shown in Scheme I.

Reaction of the bisilylated phosphorane **6** with trimethylsilyl perrhenate in THF or toluene led to a complex mixture of products (as indicated by ^{31}P NMR spectroscopy) instead of the expected metallacycle **7** (Scheme II). Hexamethyldisiloxane was identified as one of the major products in this reaction by means of the ^{29}Si NMR spectrum of the reaction mixture. It appears that the chemical lability of the three $-\text{OSiMe}_3$ groups in **7** leads to facile inter- and intramolecular eliminations of hexamethyldisiloxane resulting in complex polymeric products.

Discussion

The observation of characteristic vibrational absorptions for the $\text{P}=\text{N}$ bonds at $1250\text{--}1260\text{ cm}^{-1}$ in **2** or **4** (vs ν_{PN} for **1** or **3** of $1300\text{--}1310\text{ cm}^{-1}$) is consistent with the formation of $\text{Re}-\text{N}$ σ bonds in these metallacycles and suggests that the phosphoran-imino moiety is acting as a univalent anion bound to $\text{Re}(\text{VII})$. In contrast, formation of a simple donor-acceptor complex of the type **8** would likely have led to a greater decrease in the ν_{PN} value



in parallel with the behavior noted for a number of analogous phosphoran-imino-metal complexes¹⁴⁻¹⁷ (for example, $\nu_{\text{P}=\text{N}}$ values

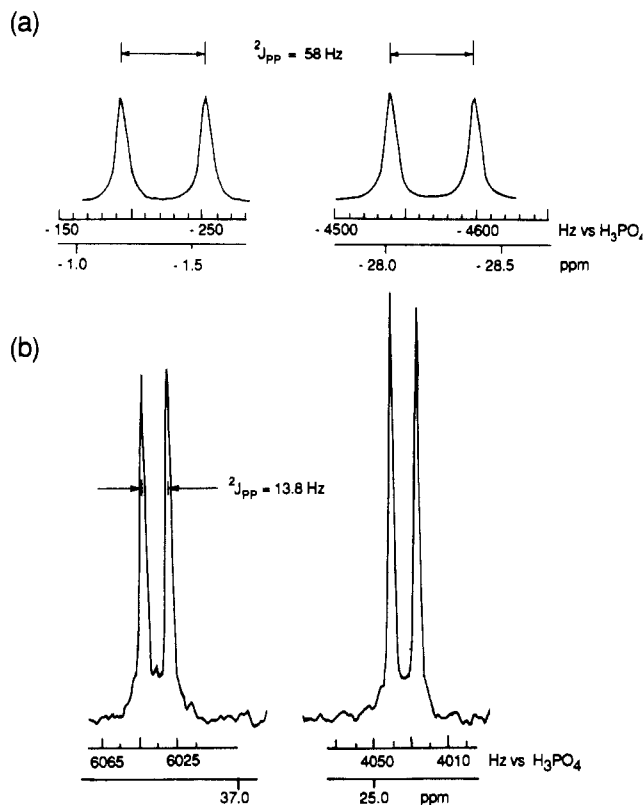
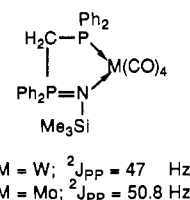


Figure 1. Proton-decoupled ^{31}P NMR spectra of (a) the phosphoranimino phosphane **1** and (b) the $\text{Re}(\text{VII})$ metallacyclic compound **2**.

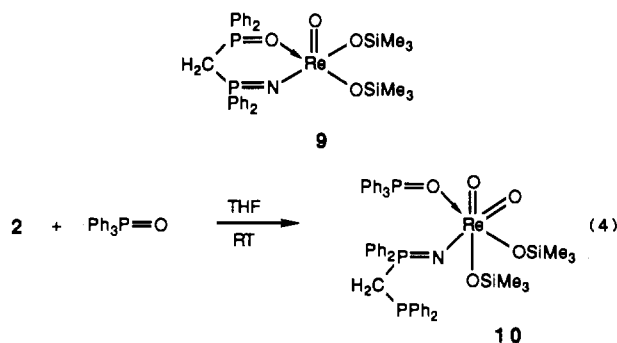
for $\text{Ph}_3\text{P}=\text{NSiMe}_3$ and its copper(I) complex are 1325 and 1109 cm^{-1} , respectively).

The ^1H -decoupled ^{31}P NMR spectrum of **2** showed two doublets typical of an AX spin pattern (Figure 1b). A significant deshielding of the phosphoran-imino and phosphane centers in **2** compared to those in **1** (Figure 1a) strongly suggests that significant interaction of the rhenium metal center with both $-\text{N}=\text{PPh}_2$ and $-\text{PPh}_2$ groups occurs. A marked decrease in the $^2J_{\text{PP}}$ value in the metallacyclic compound **2** (13 Hz) compared to the free ligand **1** (58 Hz) further suggests the withdrawal of electron density from the $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ unit by the high oxidation state of the rhenium metal center. This interpretation is supported by our spectroscopic observations for related metallacycles that contain tungsten(0) and molybdenum(0) metal centers.¹³



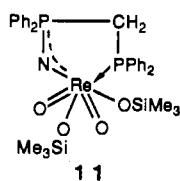
The magnitudes of the $^2J_{\text{PP}}$ values in these metallacycles showed only a modest decrease compared to the free ligand, a behavior that is consistent with the reduced ability of the electron-rich $\text{W}(\text{0})$ and $\text{Mo}(\text{0})$ metal centers to accept electron density from the ligand. An alternative $\text{Re}(\text{V})$ isomeric structure **9** that could have arisen as a result of the oxidation of phosphane unit in **2** has been ruled out by the demonstration that Ph_3PO displaces the coordinated phosphane end of the bidentate ligand under mild conditions (eq 4). The ^{31}P NMR spectrum of the light yellow Ph_3PO

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adduct **10** consisted of two doublets of an AX spin system (centered at 37.49 and -28.60 ppm; $^2J_{\text{PP}} = 61.55$ Hz)¹⁸ and a singlet at 35.40 ppm. The low- and the high-field doublets are readily assigned to the bound $\text{Ph}_2\text{P}=\text{N}-$ and the Ph_2P centers, respectively, and the latter is now uncoordinated. The singlet at 35.40 ppm is typical for a coordinated phosphane oxide and is notably different from the value demonstrated by the coordinated phosphane unit in **2**. It is clear that the phosphane unit in **2** has not been oxidized by the rhenium oxide, and so we formulate the product as a Re(VII) compound with a coordinated phosphane. The color of **2**, which is discharged when the chelate structure is disrupted, is probably the consequence of delocalization in the ring or substantial charge transfer to the metal in the chelate **2**. We rationalize the stability of **2** as a Re(VII) compound as the result of Re–N σ -bond formation that probably decreases the oxidizing ability of the rhenium oxide.

Withdrawal of electron density by the Re(VII) center and the development of some multiple-bond character in the Re–N bond system implies a resonance structure of the type **11** for **2**. The



high kinetic stability of the linear metallaphosphazenes [$\text{R}_3\text{P}=\text{N}-\text{ML}_n$] in general,¹⁹ and the metallacycle **2** in particular, may be a consequence of such metal–nitrogen multiple bonding. This enhanced M–N bond order has been supported by X-ray crystallographic data for a number of phosphoranimino–metal compounds of the type¹⁸ $\text{R}_3\text{P}=\text{N}-\text{ML}_n$. A similar resonance structure for **4** may be envisaged.

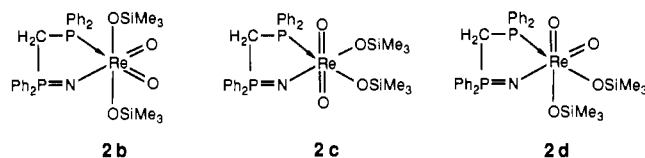
The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4** consisted of a singlet at 38.98 ppm (a value close to that observed for the phosphoranimino center in **2**), and the value indicates a substantial deshielding compared to the value of 1.83 ppm observed for the free ligand **3**. The coordination interaction between rhenium and arsenic is by no means evident due to the lack of magnetically active nuclei; however, the higher nucleophilicity of the Ph_2As center (in **3**) compared to Ph_2P center (in **1**) should favor strong Re–As interactions with the result that this six-membered-ring system should also demonstrate a kinetic stability higher than the considerable stability found for **2**.

Unambiguous evidence for the migration of the $-\text{SiMe}_3$ group from the phosphoranimine center to the rhenium–oxo center comes from the ^{29}Si NMR spectra of **2** and **4**. **2** shows two sharp singlets at 17.11 and 7.46 ppm compared to the doublet signal (centered at -12.75 ppm, $^2J_{\text{Si}-\text{P}} = 21.8$ Hz) observed for the free ligand

(18) These P^{III} and P^{V} chemical shifts and coupling constants are similar to those of metalated phosphoranimine phosphanes. For example, the corresponding values for $\text{CpTiCl}_2\text{N}=\text{PPh}_2\text{CH}_2\text{PPh}_2$ are $\sigma(\text{P}^{\text{V}})$ 38.64 and $\sigma(\text{P}^{\text{III}})$ -28.95 ppm ($^2J_{\text{PP}} = 59.73$).

(19) See for example: (a) Bezler, H.; Strahle, J. Z. *Naturforsch.* **1979**, *34b*, 1199. (b) Dilsworth, J.; Neares, B. D.; Hutchinson, J. P.; Zubieta, J. A. *Inorg. Chim. Acta* **1982**, *65*, L223. (c) Bezler, H.; Strahle, J. H. Z. *Naturforsch.* **1983**, *38b*, 317. (d) Roesky, H. W.; Seseke, U.; Noltemeyer, M.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1986**, 1309.

1. Similarly, two singlets at 18.17 and 8.23 ppm appear in the ^{29}Si NMR spectrum of **4** compared to the parent ligand **3**, which showed a doublet centered at -11.3 ppm ($^2J_{\text{Si}-\text{P}} = 19.57$ Hz). The significant deshielding of the ^{29}Si NMR resonances in **2** and **4** suggests the presence of OSiMe_3 ($\sigma(\text{Me}_3\text{SiOREO}_3)$ 18.03 ppm) rather than NSiMe_3 groups. The difference between the chemical shifts of the OSiMe_3 groups within each of these compounds excludes the symmetric *cis*-dioxo structure **2b** wherein the



trans-disposed OSiMe_3 groups would be magnetically equivalent. The *trans*-dioxo structure **2c** (which is consistent with the silicon NMR results) may be discounted on the basis of the large differences in the trans effects of the phosphorus(III) and nitrogen substituents in **2**. The structures **2a** and **2d** are consistent with the ^{29}Si NMR results and are in agreement with the general tendency of d^0 dioxo compounds of rhenium to adopt a *cis*-dioxo structure.^{3,4} The highly colored nature of **2** and **4** precludes structural elucidation via Raman spectroscopy, and the infrared spectra do not provide definitive distinctions between *cis* or *trans* geometries. Attempts to grow single crystals from either **2** or **4** have so far been unsuccessful.

Conclusion

We have demonstrated that stable Re(VII) metallacycles can be generated via Me_3Si migration from the nitrogen of a silylated phosphoranimine phosphane or arsane to the terminal oxygen of a high-valent metal oxide with concomitant formation of a metal–nitrogen σ bond. The reaction is probably assisted by cooperative interactions between the π -acid centers (P(III) or As(III)) and the basic nitrogen center, and the resultant metallacycle shows NMR spectral features suggestive of extensive delocalization involving the metal and ring atoms. The reactivity of these metallacycles is of interest, and studies are under way.

Experimental Section

Materials. All experimental manipulations were performed under an atmosphere of dry argon. Solvents were dried and distilled prior to use; $\text{Me}_3\text{SiN}=\text{PPh}_2\text{CH}_2\text{PPh}_2$ (**1**), $\text{Me}_3\text{SiOREO}_3$,²⁰ and $\text{Me}_3\text{SiN}=\text{PPh}_2\text{CH}_2\text{P}=\text{NSiMe}_3$ (**6**) were prepared according to published procedures. Re_2O_7 was obtained from Aldrich. ^1H , ^{31}P , and ^{29}Si NMR spectra were obtained by means of a Bruker WP400 instrument operating at the appropriate frequencies. ^1H and ^{29}Si NMR shifts are quoted with respect to tetramethylsilane, while ^{31}P NMR shifts are referenced to 85% H_3PO_4 . A positive sign denotes a shift downfield from that of the reference. Mass spectra were recorded on a Kratos MS50 instrument. An INEPT sequence was used to enhance ^{29}Si NMR signals.²² Molecular weights were measured in dibromomethane solutions by using a Mechrolab 301A osmometer. Microanalysis were performed in this department.

Synthesis of $\text{NPPh}_2\text{CH}_2\text{PPh}_2\text{Re}(\text{O})_2(\text{OSiMe}_3)_2$ (2**).** A solution of **1** (2.54 g; 5.39 mmol) in dry THF (50 mL) was added dropwise to a solution of $\text{Me}_3\text{SiOREO}_3$ (1.74 g; 5.39 mmol) also in THF (50 mL). The mixture was stirred at room temperature for 10 h before the solvent was removed in vacuo to yield brown crystalline analytically pure **2** (yield 4.10 g, 95%; mp 140 °C). Anal. Calcd for $\text{C}_{31}\text{H}_{40}\text{NP}_2\text{O}_4\text{Si}_2\text{Re}$: C, 46.83; H, 5.03; N, 1.76. Found: C, 46.69; H, 5.17; N, 1.74%. MS (EI, m/z): 794 (M^+). MW: calcd, 794.28; found (dibromomethane), 803. IR (Nujol, cm^{-1}): 1250 (s, br), 1220 (s), 1110 (m), 950 (m, br), 900 (s), 750 (m, br), 690 (m), 500 (m). ^{31}P NMR (161.98 MHz in CDCl_3 , ppm vs 85% H_3PO_4): $\sigma(\text{P}^{\text{III}})$ 25.45, $\sigma(\text{P}^{\text{V}})$ 36.99 ($^2J_{\text{PP}} = 13.80$ Hz). ^{29}Si NMR (INEPT; 79.5 MHz, in CDCl_3 , ppm vs Me_4Si): δ 17.11 (s), 7.46 (s). ^1H NMR (CDCl_3 , ppm): phenyl rings, δ 7.35, 7.60, 7.73 (m, 20 H); PCH_2P , δ 4.14 (dd, 2 H, $^2J_{\text{HP}} = 14.92$, 11.84 Hz); $-\text{OSi}(\text{CH}_3)_3$, δ 0.14 (s, 18 H).

Synthesis of $\text{NPPh}_2(\text{CH}_2)_2\text{AsPh}_2\text{Re}(\text{O})_2(\text{OSiMe}_3)_2$ (4**).** A solution

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of 3 (2.05 g; 3.87 mmol) in dry THF (75 mL) was added dropwise to a solution of $\text{Me}_3\text{SiOREO}_3$ (1.25 g; 3.87 mmol) also in the same solvent (50 mL). The mixture was stirred at room temperature for 10 h before the solvent was removed in vacuo to yield a brown crystalline solid. Recrystallization from toluene- CH_2Cl_2 gave pure 4 (yield 2.70 g, 81%; mp 160-162 °C). Anal. Calcd for $\text{C}_{32}\text{H}_{42}\text{NAsO}_4\text{PRE}_2\text{Si}_2$: C, 45.65; H, 4.92; N, 1.64. Found: C, 45.49; H, 4.91; N, 1.62%. MS (EI, m/z) 852 (M^+). MW: calcd, 852.20; found (dibromomethane), 870. IR (Nujol, cm^{-1}): 1260 (s, br), 1225 (s), 1115 (m), 960 (m, br), 895 (s), 780 (m), 750 (m, br), 685 (m), 505 (m). ^{31}P NMR (161.98 MHz in CDCl_3 , ppm vs 85% H_3PO_4) $\sigma(\text{P})$ 38.98 (s). ^{29}Si NMR (INEPT; 79.5 MHz, in CDCl_3 , ppm vs Me_4Si): δ 18.17 (s), 8.25 (s). ^1H NMR (CDCl_3 , ppm): phenyl rings, δ 7.36, 7.55, 7.70 (m, 20 H); $\text{AsCH}_2\text{CH}_2\text{P}$, δ 2.20 (m, 2 H), 2.61 (m, 2 H); $-\text{OSi}(\text{CH}_3)_3$, δ 0.16 (s, 18 H).

Reaction of 1 with Re_2O_7 . A solution of 1 (3.01 g; 6.30 mmol) in dry THF (50 mL) was added dropwise to a suspension of Re_2O_7 (1.55 g; 3.19 mmol) also in THF (75 mL). The mixture when stirred at room temperature for 24 h turned into a clear, dark brown solution. The solution was then concentrated (~ 50 mL) in vacuo, and an aliquot of this solution was investigated by ^{31}P NMR spectroscopy (161.98 MHz, CDCl_3 lock, ppm vs 85% H_3PO_4). 5: $\sigma(\text{P}_A)$ 72.47, $\sigma(\text{P}_X)$ 10.20 ($^2J_{\text{P}_A\text{P}_X} = 23.56$ Hz). 2: $\sigma(\text{P}^{\text{III}})$ 25.40, $\sigma(\text{P}^{\text{V}})$ 36.97 ($^2J_{\text{PP}} = 13.80$ Hz). Ratio of 5:2 from the relative integrations: 2:3.

The remainder of the concentrated solution obtained above (consisting of the mixture of 5 and 2) was treated with a solution of $(\text{Me}_3\text{Si})_2\text{O}$ (0.58 g; 3.00 mmol) in THF (20 mL) at room temperature. The mixture was stirred for 6 h before the solvent was removed in vacuo to yield a brown crystalline solid. Recrystallization from THF gave pure 2 (yield 74%). The physical constants and the spectroscopic parameters of this product were the same as listed for 2 above.

Synthesis of the Triphenylphosphine Oxide Adduct of 2. A solution of 2 (1.17 g; 1.47 mmol) in dry CH_2Cl_2 (50 mL) was added dropwise to a solution of Ph_3PO (0.41 g; 1.47 mmol) also in CH_2Cl_2 (25 mL). The reaction mixture, which changed its color from dark brown to pale yellow during the course of this addition, was stirred at room temperature for 2 h before the solvent was removed in vacuo to yield a pale yellow solid 10 (yield 1.46 g, 93%; mp 190-192 °C dec). Anal. Calcd for $\text{C}_{49}\text{H}_{55}\text{NP}_3\text{O}_5\text{Si}_2\text{Re}$: C, 54.85; H, 5.13; N, 1.30. Found: C, 54.78; H, 5.09; N, 1.29. ^{31}P NMR (161.98 MHz in CDCl_3 , ppm vs 85% H_3PO_4): $\sigma(\text{P}^{\text{V}})$ 37.49, $\sigma(\text{P}^{\text{III}})$ -28.50 ($^2J_{\text{PP}} = 61.55$ Hz); $\sigma(\text{P}^{\text{V}})(\text{Ph}_3\text{P}(\text{O}))$ 35.40. ^1H NMR (CDCl_3 , ppm): phenyl rings, δ 7.40, 7.62, 7.70 (m, 35 H); PCH_2P , δ 3.80 (dd, 2 H; $^2J_{\text{HP}^{\text{V}}} = 13.15$ Hz; $^2J_{\text{HP}^{\text{III}}} = 1.15$ Hz); $\text{OSi}(\text{C}-\text{H}_3)_3$, δ 0.12 (s, 18 H).

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Pentaammineruthenium(II), Pentaammineosmium(II), and (*N*-(Hydroxyethyl)ethylenediaminetriacetato)ruthenate(II) Complexes of Styrenes

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$[\text{M}(\text{NH}_3)_5(\text{styrene})^{2+}]$ and $[\text{M}(\text{NH}_3)_5(\text{olefin})^{2+}]$ ($\text{M} = \text{Ru}^{\text{II}}, \text{Os}^{\text{II}}$) and the related $\text{Ru}(\text{hedta})(\text{styrene})^-$ and $\text{Ru}(\text{hedta})(\text{olefin})^-$ complexes have been prepared and characterized by ^1H and ^{13}C NMR spectroscopy and by cyclic voltammetry and differential-pulse polarography. Complexes in these series include styrene, 4-vinylbenzoic acid, dimethyl acetylenedicarboxylate (DMAD), 1,3-cyclohexadiene, and 3-cyclohexene-1,1-dimethanol (CHDM). Preferential coordination of the metal centers to the exo vinylic substituent of the styrenes rather than η^2 ring coordination was observed. The chemical shifts and electrochemical behavior were found to be similar to those of linear olefin analogues such as propylene and 1,3-butadiene. ^1H NMR upfield shifts of protons of the coordinated vinylic group of styrene are virtually the same as those of the $\text{M}(\text{NH}_3)_5(1,3\text{-butadiene})^{2+}$ analogues; the greater effect of Os^{II} vs Ru^{II} is maintained. $E_{1/2}$ values for the styrene complexes were found to be 0.98 V for $(\text{NH}_3)_5\text{Ru}(\text{styrene})^{2+}$, 0.49 V for $(\text{NH}_3)_5\text{Os}(\text{styrene})^{2+}$ and 0.64 V for $(\text{hedta})\text{Ru}(\text{styrene})^-$ complexes, again similar to those for linear olefin analogues. $E_{1/2}$ values for substituted styrenes with para substituents $-\text{CO}_2\text{H}$ and $-\text{CO}_2^-$ were virtually the same (± 0.02 V) as those for the parent styrene complexes. A plot of $\Delta E_{1/2} = (E_{1/2}[\text{Ru}(\text{NH}_3)_5\text{L}] - E_{1/2}[\text{Ru}(\text{hedta})\text{L}])$ vs the π -acceptor power of L (ESCA scale) was shown to be linear with a slope of 0.325 ± 0.073 V and an intercept of 0.106 ± 0.044 V, including points for $\text{L} = \text{H}_2\text{O}$, CH_3CN , py, pz, olefins, styrenes, CO, and CH_3pz^+ . DMAD was shown to deviate from the line, which is attributed to the π -donor character of the second π lone pair available with acetylenes. The ammine environment is better than hedta^{3-} in stabilizing Ru^{II} complexes with strong π -acceptor ligands. The ^{13}C NMR spectra reveal an opposite influence of the coordination of $\text{Ru}(\text{NH}_3)_5^{2+}$ and $\text{Os}(\text{NH}_3)_5^{2+}$ moieties. The aromatic carbon attached to the vinylic substituent shifts downfield 12 ppm for Ru^{II} and upfield 8 ppm for Os^{II} . A greater involvement of the ring carbon in a "allylic-like" coordination to $(\text{NH}_3)_5\text{Os}^{2+}$ is suggested by this result.

Introduction

We recently have begun a series of studies to examine the coordination chemistry of olefins and acetylenes toward the π -base $(\text{NH}_3)_5\text{Ru}^{\text{II}}$ and $(\text{NH}_3)_5\text{Os}^{\text{II}}$ moieties.¹⁻³ This work is of general interest as the $(\text{NH}_3)_5\text{M}^{\text{II}}$ chromophore ($\text{M}^{\text{II}} = \text{Ru}^{\text{II}}, \text{Os}^{\text{II}}$) has been shown to catalyze chemical changes at unsaturated carbon centers such as decarbonylations of aldehydes,^{4,8,14} amides,⁴ and

formic acid.⁵ We have examined the coordination of dimethyl acetylenedicarboxylate (DMAD) to $(\text{NH}_3)_5\text{Ru}^{\text{II}}$ by X-ray diffraction and spectral, electrochemical, and surface science techniques.^{1,2} These studies have shown that DMAD is about 83% as good a π -acceptor ligand as CO toward $(\text{NH}_3)_5\text{Ru}^{\text{II}}$ and that the acetylenes and olefins are better π -acceptors than the N-heterocyclic pyridines and pyrazines.² The latter N-bases have been extensively studied in their complexes of $(\text{NH}_3)_5\text{Ru}^{\text{II}}$ and $(\text{NH}_3)_5\text{Os}^{\text{II}}$, largely because the N-heterocyclic complexes of these metal centers exhibit convenient MLCT transitions in the visible

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