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Communications

Labile, Reactive Bis(imido)rhenium(V) Complexes

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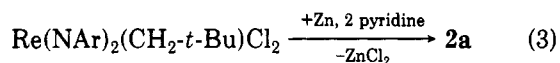
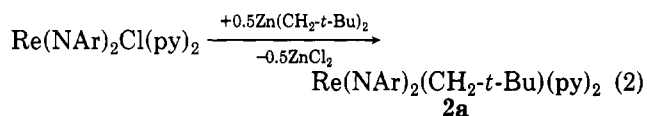
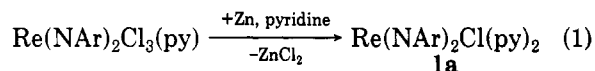
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Summary: $\text{Re}(\text{NAr})_2\text{Cl}_3(\text{py})$ ($\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{-}i\text{-Pr}_2$) reacts with 1 equiv of zinc dust in the presence of excess pyridine in tetrahydrofuran to give red-brown microcrystalline $\text{Re}(\text{NAr})_2\text{Cl}(\text{py})_2$ (**1a**) in 80% yield. Emerald green $\text{Re}(\text{NAr})_2(\text{CH}_2\text{-}t\text{-Bu})(\text{py})_2$ (**2a**) can be prepared by addition of 0.5 equiv of dineopentylzinc to **1a** in dichloromethane or by reducing $\text{Re}(\text{NAr})_2(\text{CH}_2\text{-}t\text{-Bu})\text{Cl}_2$ in the presence of pyridine. Addition of 2-butyne to **1a** or **2a** gives complexes of the form $\text{Re}(\text{ArN})_2\text{X}(2\text{-butyne})$ ($\text{X} = \text{Cl}, \text{CH}_2\text{-}t\text{-Bu}$), while addition of acetone, pivaldehyde, or norbornene to **2a** gives complexes of the form $\text{Re}(\text{NAr})_2(\text{CH}_2\text{-}t\text{-Bu})(\eta^2\text{-ligand})$. Reduction of $\text{Re}(\text{NAr})_2(\text{CH}_2\text{-}t\text{-Bu})\text{Cl}_2$ in the presence of PMe_2Ph yields $\text{Re}(\text{NAr})_2(\text{CH}_2\text{-}t\text{-Bu})(\text{PMe}_2\text{Ph})$.

Although mono(imido) complexes of rhenium(V) have been known for some time,^{1,2} there appears to be no published example of a bis(imido)rhenium(V) complex. The recent discovery of labile tungsten(IV) bis(imido) complexes³ suggested that analogous labile rhenium(V) species should be preparable. We report such species here.

$\text{Re}(\text{NAr})_2\text{Cl}_3(\text{py})$ ($\text{NAr} = 2,6\text{-C}_6\text{H}_3\text{-}i\text{-Pr}_2$) is reduced by 1 equiv of zinc in the presence of excess pyridine in tetrahydrofuran to give red-brown microcrystalline $\text{Re}(\text{NAr})_2\text{Cl}(\text{py})_2$ (**1a**) in 80% yield (eq 1). Addition of 0.5



equiv of dineopentylzinc to **1a** in dichloromethane yields extremely air-sensitive, emerald green $\text{Re}(\text{NAr})_2(\text{CH}_2\text{-}t\text{-Bu})(\text{py})_2$ (**2a**) in good yield (eq 2). Alternatively, **2a** can be prepared by zinc reduction of $\text{Re}(\text{NAr})_2(\text{CH}_2\text{-}t\text{-Bu})\text{Cl}_2$ in the presence of pyridine (eq 3). All NMR data are consistent with **1a** and **2a** being trigonal bipyramids that contain axial pyridine ligands and aryl rings which lie in the equatorial plane in the lowest energy configuration, a type of structure that has been observed recently for d^2 $\text{Os}(\text{NAr})_2(\text{PMe}_2\text{Ph})\text{I}_2$.⁵ NMR studies show that exchange of free with coordinated pyridine in **2a** is slow on the NMR time scale up to 70 °C, although added pyridine- d_5 exchanges in 15 min or less with coordinated pyridine in **1a** and **2a** at 25 °C. In **1a** and **2a** the two imido ligands can form only three π -bonds to the metal to give formally 18-electron species.^{2,6}

2-Butyne reacts rapidly with **1a** and **2a** to give complexes of the form $\text{Re}(\text{ArN})_2\text{X}(2\text{-butyne})$ ($\text{X} = \text{Cl}$ (**1b**), $\text{CH}_2\text{-}t\text{-Bu}$ (**2b**), eq 4). In NMR spectra of **1b** and **2b** the imido

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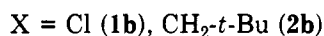
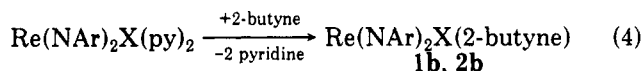
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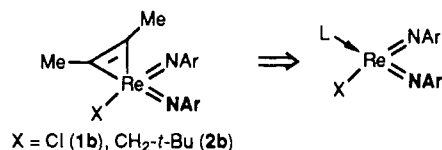
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ligands are equivalent and the ends of the coordinated 2-butyne are inequivalent, and in **2b** the methylene protons of the neopentyl ligand are equivalent. These data suggest that X, 2-butyne, and Re lie in the same plane, one that bisects the N-Re-N angle in the pseudotetrahedral species. This type of structure has been observed for the isoelectronic dioxo complexes $\text{ReO}_2(\text{RC}\equiv\text{CR})\text{R}'$,⁷ one of which has been structurally characterized,^{7b} but the origin of the structure was not explained in this fashion.



Analogous reactions between **2a** and acetone, pivaldehyde, or norbornene (NBE) give yellow-brown $\text{Re}(\text{NAr})_2(\text{CH}_2\text{-}t\text{-Bu})(\eta^2\text{-OCMe}_2)$ (**2c**), $\text{Re}(\text{NAr})_2(\text{CH}_2\text{-}t\text{-Bu})(\eta^2\text{-OCH}_2\text{-}t\text{-Bu})$ (**2d**), and $\text{Re}(\text{NAr})_2(\text{CH}_2\text{-}t\text{-Bu})(\text{NBE})$ (**2e**), respectively. No ν_{CO} stretch is observed for **2c** or **2d** above 1450 cm^{-1} . NMR spectra again are consistent with a rigid pseudotetrahedral core geometry in which the π -bound ligand does not rotate about the ligand(centroid)-metal axis. Compounds **2c-e** are analogous to those recently reported for tungsten(IV) bis(imido) complexes having the $\text{W}(\text{NAr})_2(\text{PMe}_2\text{Ph})$ core instead of the $\text{Re}(\text{NAr})_2\text{X}$ core;³ the structure of $\text{W}(\text{NAr})_2(\text{PMe}_2\text{Ph})(\eta^2\text{-OCMe}_2)$ has been determined.³

$\text{Re}(\text{NAr})_2(\text{CH}_2\text{-}t\text{-Bu})\text{Cl}_2$ can be reduced in the presence of PMe_2Ph to give highly crystalline, diamagnetic $\text{Re}(\text{NAr})_2(\text{CH}_2\text{-}t\text{-Bu})(\text{PMe}_2\text{Ph})_2$ (**2f**) in high yield. It is presumably a pseudotetrahedral relative of $\text{W}(\text{NAr})_2(\text{PMe}_2\text{Ph})_2$, and it reacts with 2-butyne to give **2b**.

All the above pseudotetrahedral bis(imido) complexes could be viewed as 18-electron complexes that contain four metal-imido π -bonds. The $16e \text{ Re}(\text{NAr})_2\text{X}$ fragment, therefore, is isolobal and isoelectronic with MCp_2X ($\text{M} = \text{Nb}, \text{Ta}$; X = monoanionic ligand), if the imido ligands are counted as $6e$ dianionic $2\pi, 1\sigma$ -electron donors. We believe that $\text{Re}(\text{NAr})_2\text{X}(\text{py})_2$ species react with π ligands via loss of pyridine to give $\text{Re}(\text{NAr})_2\text{X}(\text{py})$, although associative processes cannot be ruled out at this stage.

Two NAr ligands contribute a significant amount of bulk to the coordination sphere. They are not as likely to bridge between metals as oxo ligands and thereby discourage potentially complicating bimolecular reactions. They also may discourage formation of six-coordinate bis(imido) complexes⁸ and therefore maintain the system in the four-/five-coordinate manifold. Note that pseudotetrahedral bis(imido) complexes are related to imido alkylidene complexes containing bulky ligands such as $\text{Mo}(\text{CH}_2\text{-}t\text{-Bu})(\text{NAr})(\text{OR})_2$,⁹ which also react relatively readily (e.g., with olefins¹⁰) via five-coordinate intermediates.

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Acknowledgment. We thank the National Science Foundation (Grant No. CHE 88-22508) for research support and for a predoctoral fellowship to I.A.W. and the National Institutes of Health for a postdoctoral fellowship to W.E.C.

Supplementary Material Available: A description of synthetic procedures, NMR data, and analytical data (4 pages). Ordering information is given on any current masthead page.

(8) Preliminary studies (I.A.W.) suggest that $\text{Re}(\text{NAr})_2\text{Cl}(\text{py})_2$ reacts with AgBF_4 in methylene chloride in the presence of pyridine to give $\text{trans-}[\text{Re}(\text{NAr})_2(\text{py})_4][\text{BF}_4]$.

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Transition-Metal-Substituted Diphosphenes. 22.¹ Cycloaddition Reactions of the Diphosphenyl Complex $(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{Fe-P=P-Mes}^*$ ($\text{Mes}^* = 2,4,6\text{-}t\text{Bu}_3\text{C}_6\text{H}_2$) with Azodicarboxylates. X-ray Structure Analysis of $(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{Fe-P(=P-Mes}^*)[\text{N}(\text{CO}_2\text{Et})\text{N}=\text{C}(\text{OEt})\text{O}]$

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Summary: The diphosphenyl complex $(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{Fe-P=P-Mes}^*$ ($\text{Mes}^* = 2,4,6\text{-}t\text{Bu}_3\text{C}_6\text{H}_2$) undergoes a [1 + 4] cheletropic cycloaddition with the azodicarboxylates $\text{RO}_2\text{C-N=N-CO}_2\text{R}$ ($\text{R} = \text{Et}, t\text{Bu}$) to give the metal-substituted oxadiazaphosphenes $(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{Fe-P(=P-Mes}^*)[\text{N}(\text{CO}_2\text{R})\text{N}=\text{C}(\text{OR})\text{O}]$ with exocyclic P=P bonds. The molecular structure of one of the compounds ($\text{R} = \text{Et}$) was elucidated by a single-crystal X-ray analysis.

Electron-releasing organometallic substituents considerably enhance the nucleophilicity of a diphosphene. In molecules such as $(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{M-P=P-Mes}^*$ ($\text{Mes}^* = 2,4,6\text{-}t\text{Bu}_3\text{C}_6\text{H}_2$; $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$) the HOMO is mainly represented by the lone pair at the metalated phosphorus atom. This is documented by a number of reactions of $(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{Fe-P=P-Mes}^*$ (**1**) with organic and organometallic electrophiles. The treatment of **1** with acrolein, methacrolein, and methyl vinyl ketone leads to oxaphosphenes **I**.²

With fumarodinitrile, maleodinitrile, dimethyl fumarate, and dimethyl maleate **1** generates all-trans-configured

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