

path corresponds to the main one found when Fe<sub>3</sub>(CO)<sub>12</sub> alone is reacted with PhC<sub>2</sub>Ph.

The detection of just one isomer of formula Fe<sub>2</sub>Ru(CO)<sub>9</sub>(alkyne) has been accounted for in terms of the leading role of the electronic effects with respect to the

steric factors. Furthermore its formation by thermal reaction of Fe<sub>3</sub>(CO)<sub>9</sub>(alkyne) with Ru<sub>3</sub>(CO)<sub>12</sub> suggests that a possible pathway in the reaction of Fe<sub>3</sub>(CO)<sub>12</sub> with alkynes passes through a binuclear intermediate containing an iron-iron double bond. It has also been shown that the I → III transformation occurs with the preservation of the cluster integrity.

Finally we wish to emphasize that, apart from the intrinsic interest to synthesize novel heterometallic clusters, the study of reactions involving different metal carbonyl substrates can provide a fruitful source of mechanistic information in the reaction between M<sub>3</sub>(CO)<sub>12</sub> and alkynes.

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**Supplementary Material Available:** Tables of structure factor amplitudes, fractional coordinates, and thermal parameters for (C<sub>6</sub>H<sub>5</sub>C<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)Ru<sub>1</sub>Fe<sub>2</sub>(CO)<sub>9</sub> (19 pages). Ordering information is given on any current masthead page.

## A Rarely Encountered Class of Stable Mononuclear 17-Electron Rhenium(II) Complexes: *trans*-[Re(CNR)<sub>2</sub>(NCCH<sub>3</sub>)L(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (R = *i*-Pr or *t*-Bu and L = CH<sub>3</sub>CN or py)

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The reactions of [ReH(NCCH<sub>3</sub>)<sub>3</sub>L(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (L = CH<sub>3</sub>CN, py, C<sub>6</sub>H<sub>11</sub>NH<sub>2</sub>, or *t*-BuNH<sub>2</sub>) with RNC (R = *i*-Pr or *t*-Bu) proceed in a stepwise fashion to afford [ReH(NCCH<sub>3</sub>)<sub>2</sub>(CNR)L(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (I), [Re(CNR)<sub>2</sub>(NCCH<sub>3</sub>)L(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (II), and [Re(CNR)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (III). Complexes of the type II are oxidized to the corresponding paramagnetic 17-electron dications. The crystal structure of the dichloromethane solvate of [Re(CN-*t*-Bu)<sub>2</sub>(NCCH<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> shows it to be the all-*trans* isomer. It crystallizes in a unit cell with *a* = 44.729 (2) Å, *b* = 12.170 (1) Å, *c* = 21.018 (2) Å, β = 106.15 (2)°, *V* = 10.989 Å<sup>3</sup>, *Z* = 8, and monoclinic space group *C*2/*c*.

### Introduction

Well-defined and structurally characterized mononuclear coordination complexes of Re(II) are rare,<sup>2,3</sup> although the stability of this oxidation state can be engendered through the formation of rhenium-rhenium multiple bonds as in the dirhenium(II) complexes Re<sub>2</sub>X<sub>4</sub>(PR<sub>3</sub>)<sub>4</sub> (X = halide).<sup>4,5</sup> The rarity of such mononuclear species is especially surprising in view of the stability of other d<sup>5</sup> complexes such as those of Mn(II) and Os(III). In this report we describe details of the isolation of members of a new class of mononuclear paramagnetic 17-electron

rhenium(II) complex, viz., [Re(CNR)<sub>2</sub>(NCCH<sub>3</sub>)L(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, where R = *i*-Pr or *t*-Bu and L = CH<sub>3</sub>CN or py, that we have obtained during our investigations into the reactivity of the rhenium(III) monohydrides [ReH(NCCH<sub>3</sub>)<sub>3</sub>L(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, where L = CH<sub>3</sub>CN, py, C<sub>6</sub>H<sub>11</sub>NH<sub>2</sub>, or *t*-BuNH<sub>2</sub>,<sup>6</sup> a group of molecules that are iso-electronic with several related cationic hydrido species of Mo(IV), W(IV), and Ir(III).<sup>7-10</sup> Details of the crystal

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(10) The closely related seven-coordinate rhenium(III) monohydride complex [ReHCl(PMe<sub>3</sub>)<sub>5</sub>](BF<sub>4</sub>) has recently been the subject of a study by Wilkinson and co-workers; see: Chiu, K. W.; Howard, C. G.; Rzepa, H. S.; Sheppard, R. N.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *Polyhedron* **1982**, *1*, 441.

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structure of one of these derivatives, namely, the all-trans isomer  $[\text{Re}(\text{CN-}t\text{-Bu})_2(\text{NCCH}_3)_2(\text{PPh}_3)_2](\text{BF}_4)_2$ , are also reported.

### Experimental Section

**Starting Materials.** The monohydrido complexes  $[\text{ReH}(\text{NCCH}_3)_3\text{L}(\text{PPh}_3)_2](\text{BF}_4)_2$ , where  $\text{L} = \text{CH}_3\text{CN}$ ,  $\text{py}$ , or  $\text{C}_6\text{H}_{11}\text{NH}_2$ , were prepared by the method we have described previously.<sup>6</sup> The analogous *tert*-butylamine derivative  $[\text{ReH}(\text{NCCH}_3)_3(\text{NH}_2\text{-}t\text{-Bu})(\text{PPh}_3)_2](\text{BF}_4)_2$ , which is reported here for the first time, was prepared (in 81% yield) by using the same general procedure,<sup>6</sup> namely, treatment of a slurry of  $\text{ReH}_5(\text{PPh}_3)_2(\text{NH}_2\text{-}t\text{-Bu})$  in acetonitrile with  $\text{HBF}_4\cdot\text{Et}_2\text{O}$ .<sup>11</sup>

**Reaction Procedures.** All reactions were carried out under an atmosphere of nitrogen.

**A. The Reactions of  $[\text{ReH}(\text{NCCH}_3)_3\text{L}(\text{PPh}_3)_2](\text{BF}_4)_2$  ( $\text{L} = \text{CH}_3\text{CN}$  or  $\text{C}_5\text{H}_5\text{N}$ ) with Alkyl Isocyanides.** (i)  $[\text{Re}(\text{CN-}t\text{-Bu})_2(\text{NCCH}_3)_2(\text{PPh}_3)_2](\text{BF}_4)_2$  and  $[\text{Re}(\text{CN-}t\text{-Bu})_2(\text{NCCH}_3)_2(\text{PPh}_3)_2]\text{BF}_4$ . A mixture of  $[\text{ReH}(\text{NCCH}_3)_3(\text{PPh}_3)_2](\text{BF}_4)_2$  (0.250 g, 0.24 mmol) and *tert*-butyl isocyanide (0.10 mL, 0.94 mmol) was refluxed for 0.5 h in 1,2-dichloroethane. During this time the yellow solution turned a deep red-purple. The solvent was then removed under reduced pressure and the resulting oil dissolved in 4 mL of acetone to which was added diethyl ether until a turbidity was induced. When the solution was maintained at  $-10^\circ\text{C}$  for 3 h, purple crystals of  $[\text{Re}(\text{CN-}t\text{-Bu})_2(\text{NCCH}_3)_2(\text{PPh}_3)_2](\text{BF}_4)_2$  were obtained. These were filtered off and dried in vacuo; yield 0.106 g (39%). Recrystallization from dichloromethane-diethyl ether gave the complex as its dichloromethane solvate. Anal. Calcd for  $\text{C}_{51}\text{H}_{56}\text{B}_2\text{Cl}_2\text{F}_8\text{N}_4\text{P}_2\text{Re}$ : C, 50.30; H, 4.60. Found: C, 50.09; H, 4.89. The presence of  $\text{CH}_2\text{Cl}_2$  in the crystals of this paramagnetic complex was confirmed by  $^1\text{H}$  NMR spectroscopy ( $\delta +5.35$ ) on a  $(\text{CD}_3)_2\text{CO}$  solution.

The red filtrate that remained following harvesting of the purple crystals was chromatographed on silica gel. Elution of the red band with acetone afforded an orange powder when the acetone solution was stripped to dryness under a stream of  $\text{N}_2(\text{g})$  and the resulting oil stirred under diethyl ether (20 mL); yield 0.13 g (50%). Microanalytical data and the spectroscopic and electrochemical properties of this product showed it to be the diamagnetic 18-electron rhenium(I) complex  $[\text{Re}(\text{CN-}t\text{-Bu})_2(\text{NCCH}_3)_2(\text{PPh}_3)_2]\text{BF}_4$ . Anal. Calcd for  $\text{C}_{50}\text{H}_{54}\text{BF}_4\text{N}_4\text{P}_2\text{Re}$ : C, 57.41; H, 5.16. Found: C, 57.25; H, 5.41.

(ii)  $[\text{Re}(\text{CN-}i\text{-Pr})_2(\text{NCCH}_3)_2(\text{PPh}_3)_2](\text{BF}_4)_2$  and  $[\text{Re}(\text{CN-}i\text{-Pr})_2(\text{NCCH}_3)_2(\text{PPh}_3)_2]\text{BF}_4$ . Using a procedure analogous to A(i) and substituting isopropyl isocyanide for *tert*-butyl isocyanide produces purple crystals of  $[\text{Re}(\text{CN-}i\text{-Pr})_2(\text{NCCH}_3)_2(\text{PPh}_3)_2](\text{BF}_4)_2$ , yield 35%. Anal. Calcd for  $\text{C}_{48}\text{H}_{50}\text{B}_2\text{F}_8\text{N}_4\text{P}_2\text{Re}$ : C, 52.16; H, 4.53. Found: C, 52.08; H, 4.83.

(11) This complex was identified on the basis of its spectroscopic and electrochemical properties that were very similar to those exhibited by other complexes of the type  $[\text{ReH}(\text{NCCH}_3)_3\text{L}(\text{PPh}_3)_2](\text{BF}_4)_2$ .<sup>6</sup> Of particular note are the NMR spectral properties of these four complexes ( $\text{L} = \text{CH}_3\text{CN}$ ,  $\text{py}$ ,  $\text{C}_6\text{H}_{11}\text{NH}_2$ , and  $t\text{-BuNH}_2$ ).  $^1\text{H}$  NMR spectroscopy (at 90 MHz using a Perkin-Elmer R-32 spectrometer;  $T = +35$  to  $-60^\circ\text{C}$ ;  $\text{CD}_2\text{Cl}_2$  or  $\text{CDCl}_3$  as solvents with resonances referenced internally to residual protons therein) showed evidence for a rigid seven-coordinate structure in solution, with two methyl singlets ( $\delta$  2.50–2.40 and 2.20–1.90) signifying inequivalent  $\text{CH}_3\text{CN}$  ligands (intensity ratio 1:1 for  $\text{L} = \text{CH}_3\text{CN}$  and 2:1 for  $\text{L} = \text{py}$ ,  $\text{C}_6\text{H}_{11}\text{NH}_2$ , and  $t\text{-BuNH}_2$ ) and the Re–H resonance appearing as an apparent triplet ( $J(\text{P-H}) \approx 65$  Hz), although in actuality it is best described as a doublet of doublets. Confirmation of the latter situation was apparent upon examining the  $^{31}\text{P}$  NMR spectrum of  $[\text{ReH}(\text{NCCH}_3)_3\text{py}(\text{PPh}_3)_2](\text{BF}_4)_2$  (Varian XL-200 spectrometer at 80.98 MHz with an internal deuterium lock;  $(\text{CD}_3)_2\text{CO}$  as solvent and  $\text{P}(\text{OMe})_3$  as an external standard). Two well-defined proton-decoupled phosphorus resonances (due to inequivalent phosphine ligands) were observed at  $\delta +26.7$  and  $+23.7$  each of which appeared as a broad doublet ( $J(\text{P-H}) \approx 75\text{--}60$  Hz) in the nonproton decoupled mode. Note that the  $^{31}\text{P}$  NMR spectra of  $\text{CD}_3\text{CN}$  solutions of  $[\text{ReH}(\text{NCCH}_3)_3(\text{PPh}_3)_2](\text{BF}_4)_2$  and  $[\text{ReH}(\text{NCCH}_3)_3(\text{PMe}_2\text{Ph})_3](\text{BF}_4)_2$  are quite different<sup>7,12</sup> from that which we observe in  $(\text{CD}_3)_2\text{CO}$ . We plan to publish in due course a paper describing in detail the synthesis and properties of such monohydrido complexes of rhenium(III).

(12) Note that the paper by Crabtree and co-workers<sup>7</sup> describes the isolation and spectroscopic characterization of two rhenium hydride complexes, viz.,  $[\text{ReH}(\text{NCCH}_3)_4(\text{PPh}_3)_2](\text{BF}_4)_2$  (i.e. the same complex as that described by us in ref 6) and  $[\text{ReH}(\text{NCCH}_3)_3(\text{PMe}_2\text{Ph})_3](\text{BF}_4)_2$ .

Orange microcrystalline  $[\text{Re}(\text{CN-}i\text{-Pr})_2(\text{NCCH}_3)_2(\text{PPh}_3)_2]\text{BF}_4$  can be obtained in 57% yield by using a workup procedure similar to that described in A(i). Anal. Calcd for  $\text{C}_{48}\text{H}_{50}\text{BF}_4\text{N}_4\text{P}_2\text{Re}$ : C, 56.63; H, 4.92. Found: C, 55.77; H, 5.41.

(iii)  $[\text{Re}(\text{CN-}t\text{-Bu})_2(\text{NCCH}_3)(\text{C}_5\text{H}_5\text{N})(\text{PPh}_3)_2](\text{BF}_4)_2$  and  $[\text{Re}(\text{CN-}t\text{-Bu})_2(\text{NCCH}_3)(\text{C}_5\text{H}_5\text{N})(\text{PPh}_3)_2]\text{BF}_4$ . Red crystals of  $[\text{Re}(\text{CN-}t\text{-Bu})_2(\text{NCCH}_3)(\text{C}_5\text{H}_5\text{N})(\text{PPh}_3)_2](\text{BF}_4)_2$  can be obtained by a procedure analogous to A(i) using  $[\text{ReH}(\text{NCMe})_3(\text{C}_5\text{H}_5\text{N})(\text{PPh}_3)_2](\text{BF}_4)_2$  as starting material; yield 42%. Anal. Calcd for  $\text{C}_{53}\text{H}_{56}\text{B}_2\text{F}_8\text{N}_4\text{P}_2\text{Re}$ : C, 54.35; H, 4.79. Found: C, 53.57; H, 4.90.

$[\text{Re}(\text{CN-}t\text{-Bu})_2(\text{NCCH}_3)(\text{C}_5\text{H}_5\text{N})(\text{PPh}_3)_2]\text{BF}_4$  can be obtained as a yellow-green powder from the yellow filtrate of the preceding reaction; yield 40%. This complex was identified on the basis of its electrochemical and spectroscopic properties.

(iv)  $[\text{Re}(\text{CN-}i\text{-Pr})_2(\text{NCCH}_3)(\text{C}_5\text{H}_5\text{N})(\text{PPh}_3)_2](\text{BF}_4)_2$  and  $[\text{Re}(\text{CN-}i\text{-Pr})_2(\text{NCCH}_3)(\text{C}_5\text{H}_5\text{N})(\text{PPh}_3)_2]\text{BF}_4$ . Starting with  $[\text{ReH}(\text{NCCH}_3)_3(\text{C}_5\text{H}_5\text{N})(\text{PPh}_3)_2](\text{BF}_4)_2$  and isopropyl isocyanide and using a procedure analogous to A(i) affords  $[\text{Re}(\text{CN-}i\text{-Pr})_2(\text{NCCH}_3)(\text{C}_5\text{H}_5\text{N})(\text{PPh}_3)_2](\text{BF}_4)_2$  as red microcrystals; yield 45%. Anal. Calcd for  $\text{C}_{51}\text{H}_{52}\text{B}_2\text{F}_8\text{N}_4\text{P}_2\text{Re}$ : C, 53.58; H, 4.55. Found: C, 53.24; H, 4.74.

The complex  $[\text{Re}(\text{CN-}i\text{-Pr})_2(\text{NCMe})(\text{C}_5\text{H}_5\text{N})(\text{PPh}_3)_2]\text{BF}_4$  can be obtained as a bright-yellow powder from the reaction filtrate by using a procedure analogous to A(i); yield 49%. This complex was identified on the basis of its electrochemical and spectroscopic properties.

**B. The Reactions of  $[\text{ReH}(\text{NCCH}_3)_3\text{L}(\text{PPh}_3)_2](\text{BF}_4)_2$  ( $\text{L} = \text{CH}_3\text{CN}$ ,  $\text{C}_5\text{H}_5\text{N}$ ) with *tert*-Butyl Isocyanide in Ethanol.** A mixture of 0.20 g of  $[\text{ReH}(\text{NCCH}_3)_3\text{L}(\text{PPh}_3)_2](\text{BF}_4)_2$  ( $\text{L} = \text{CH}_3\text{CN}$  or  $\text{C}_5\text{H}_5\text{N}$ ) and 0.10 mL of *tert*-butyl isocyanide was refluxed for 3 h in 20 mL of ethanol. The solvent was then removed from the yellow solution under reduced pressure, and the residue was recrystallized from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  to afford  $[\text{Re}(\text{CN-}t\text{-Bu})_4(\text{PPh}_3)_2]\text{BF}_4$  as a light yellow powder; yield 85%. This complex was identified on the basis of the similarities of its electrochemical and spectroscopic properties with those of an authentic sample.<sup>13</sup>

**C. The Reaction of  $[\text{ReH}(\text{NCCH}_3)_3(\text{NH}_2\text{-}t\text{-Bu})(\text{PPh}_3)_2](\text{BF}_4)_2$  with *tert*-Butyl Isocyanide.** (i) **Room Temperature.** A solution of  $[\text{ReH}(\text{NCCH}_3)_3(\text{NH}_2\text{-}t\text{-Bu})(\text{PPh}_3)_2](\text{BF}_4)_2$  (0.20 g, 0.18 mmol) in 10 mL of  $\text{C}_2\text{H}_4\text{Cl}_2$  was treated with 0.10 mL (0.94 mmol) of *tert*-butyl isocyanide and the mixture stirred for 1 h at room temperature. The solvent was then removed under reduced pressure and the yellow residue recrystallized from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  to afford yellow crystals of  $[\text{ReH}(\text{NCCH}_3)_2(\text{CN-}t\text{-Bu})(\text{NH}_2\text{-}t\text{-Bu})(\text{PPh}_3)_2](\text{BF}_4)_2$ ; yield 0.172 g (83%). Anal. Calcd for  $\text{C}_{51}\text{H}_{59}\text{B}_2\text{F}_8\text{N}_4\text{P}_2\text{Re}$ : C, 53.25; H, 5.14. Found: C, 52.44; H, 5.37.

(ii) **Elevated Temperature.** A reaction mixture analogous to that described in C(i) was refluxed for 0.5 h, during which time the solution took on a golden yellow color. A similar workup procedure as described in C(i) afforded tan crystals of  $[\text{Re}(\text{CN-}t\text{-Bu})_4(\text{PPh}_3)_2]\text{BF}_4$ ; yield 80%. This complex was identified by comparison of its electrochemical and spectroscopic properties with those of an authentic sample.<sup>13</sup>

**D. The Reaction of  $[\text{ReH}(\text{NCCH}_3)_3(\text{NH}_2\text{-}t\text{-Bu})(\text{PPh}_3)_2](\text{BF}_4)_2$  with *tert*-Butyl Isocyanide.** (i) **Room Temperature.** A procedure analogous to C(i) but using  $[\text{ReH}(\text{NCCH}_3)_3(\text{NH}_2\text{-}t\text{-Bu})(\text{PPh}_3)_2](\text{BF}_4)_2$  as starting material afforded a mixture of  $[\text{Re}(\text{CN-}t\text{-Bu})_4(\text{PPh}_3)_2]^+$  and  $[\text{ReH}(\text{NCCH}_3)_2(\text{CN-}t\text{-Bu})(\text{NH}_2\text{-}t\text{-Bu})(\text{PPh}_3)_2]^{2+}$  (ca. 3:1 ratio) as determined by cyclic voltammetry (see Results and Discussion).

(ii) **Elevated Temperature.** With  $[\text{ReH}(\text{NCCH}_3)_3(\text{NH}_2\text{-}t\text{-Bu})(\text{PPh}_3)_2](\text{BF}_4)_2$  as starting material and a procedure analogous to C(ii) gave  $[\text{Re}(\text{CN-}t\text{-Bu})_4(\text{PPh}_3)_2]^+$  in high yield (85%). This complex was identified on the basis of its electrochemical and spectroscopic properties.<sup>13</sup>

**X-ray Crystallography.** Crystals of the hemisolvate  $[\text{Re}(\text{CN-}t\text{-Bu})_2(\text{NCCH}_3)_2(\text{PPh}_3)_2](\text{BF}_4)_2 \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$  were obtained by recrystallizing the crude reaction product (see section A(i)) from

(13) Salts of the *trans*- $[\text{Re}(\text{CNR})_4(\text{PR}_3)_2]^+$  cations have been isolated previously and characterized both by IR and  $^1\text{H}$  NMR spectroscopy and by cyclic voltammetry; see: Allison, J. D.; Wood, T. E.; Wild, R. E.; Walton, R. A. *Inorg. Chem.* 1982, 21, 3540.

Table I. Positional Parameters for the Nongroup Atoms of [Re(CNCMe<sub>3</sub>)<sub>2</sub>(NCCH<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>·1/2CH<sub>2</sub>Cl<sub>2</sub>

atom	x	y	z
Re	0.131025 (7)	0.20660 (3)	0.05508 (1)
P1	0.17849 (5)	0.3188 (2)	0.08240 (10)
P2	0.08361 (5)	0.0956 (2)	0.0241 (1)
Cl	0.0109 (2)	0.3440 (8)	0.1955 (4)
N1	0.1341 (2)	0.1891 (5)	-0.0403 (3)
CN11	0.1362 (2)	0.1786 (7)	-0.0925 (4)
CN12	0.1386 (3)	0.165 (1)	-0.1607 (7)
N2	0.1270 (2)	0.2260 (5)	0.1495 (3)
CN21	0.1242 (2)	0.2420 (8)	0.2100 (4)
CN22	0.1203 (3)	0.2671 (10)	0.2658 (6)
C10	0.1043 (2)	0.3433 (7)	0.0362 (4)
N10	0.0893 (2)	0.4206 (6)	0.0336 (4)
C11	0.0683 (3)	0.5184 (10)	0.0320 (5)
C12	0.0896 (3)	0.615 (1)	0.0641 (7)
C13	0.0474 (4)	0.482 (1)	0.0745 (8)
C14	0.0520 (4)	0.540 (1)	-0.0394 (8)
C20	0.1579 (2)	0.0730 (7)	0.0900 (4)
N20	0.1724 (2)	-0.0011 (6)	0.1145 (4)
C21	0.1934 (3)	-0.0908 (9)	0.1481 (6)
C22	0.2066 (4)	-0.141 (2)	0.0989 (9)
C23	0.2211 (4)	-0.034 (1)	0.2006 (8)
C24	0.1776 (4)	-0.150 (2)	0.1927 (9)
B1	0.4160 (5)	0.083 (2)	0.2129 (10)
F11	0.3947 (3)	0.095 (2)	0.2444 (8)
F12	0.4191 (4)	-0.019 (1)	0.2036 (9)
F13	0.4068 (3)	0.131 (1)	0.1548 (5)
F14	0.4433 (3)	0.120 (1)	0.2478 (6)
B2	0.1944 (5)	0.071 (2)	0.3748 (10)
F21	0.2079 (3)	-0.0162 (9)	0.3647 (6)
F22	0.1735 (3)	0.103 (1)	0.3289 (8)
F23	0.2162 (3)	0.145 (1)	0.4043 (8)
F24	0.1796 (3)	0.038 (2)	0.4214 (7)
C-S	0	0.431 (2)	1/4

<sup>a</sup> Estimated standard deviations in the last figure(s) are given in parentheses in this and all subsequent tables.

dichloromethane-diethyl ether. A rectangular prism of dimensions 0.32 × 0.18 × 0.16 mm was mounted on the tip of a glass fiber with the long axis of the crystal approximately parallel with the fiber. Indexing and data collection were done by an Enraf-Nonius CAD4 fully automatic, four-circle diffractometer using Mo K $\alpha$  radiation. The unit cell determined from the least-squares fit of 25 random reflections was  $a = 44.729$  (2) Å,  $b = 12.170$  (1) Å,  $c = 21.018$  (2) Å,  $\beta = 106.15$  (2)°, and  $V = 10.989$  (2) Å<sup>3</sup>. For  $Z = 8$ , the calculated density is 1.42 g/cm<sup>3</sup>.

Data were collected at 22 °C by using previously described techniques.<sup>14</sup> Of the 6964 unique reflections collected, only the 6036 reflections with  $F^2 > 3\sigma(F^2)$  were used in the refinement. The calculated linear absorption coefficient was 25.1 cm<sup>-1</sup>.  $\psi$ -scans on nine reflections with  $\chi$  near 90° and with values of  $2\theta$  from 5 to 22° displayed less than 10% variation. An empirical absorption correction using Flack's CAMEL JOCKEY WITH THREE HUMPS<sup>15</sup> was applied to account for the spherical absorption correction. The systematic absences ( $hkl$ ,  $h + k = 2n + 1$ ;  $h0l$ ;  $l = 2n + 1$ ) were unique for the space group  $C2/c$  or  $Cc$ . Refinement was carried out satisfactorily in  $C2/c$ .

The structure was refined by using least-squares techniques. The position of the rhenium atom was obtained from the Patterson map. All the other atoms were located from subsequent difference Fourier maps during refinement. Corrections for anomalous dispersion were included in the scattering factor tables for the rhenium, chlorine, and phosphorous atoms. The six phenyl groups of the two triphenylphosphine ligands were refined as rigid groups where each carbon-carbon bond was 1.40 Å long with bond angles of 120°. Each carbon atom in the group had its own temperature factor that was refined. In the final cycles the rhenium, chlorine, phosphorous, and fluorine atoms were refined anisotropically. The final residuals were  $R = 0.047$  and  $R_w = 0.067$ . The largest peak in the final difference Fourier was 0.469 e/Å<sup>3</sup>. The final coordinates for the nongroup atoms are listed in Table

I while the positions and thermal parameters for the rigid groups are given in Table II. A table of thermal parameters for the nongroup atoms (Table III) and a listing of observed and calculated structure factors (Table IV) are available as supplementary material.

**Physical Measurements.** Infrared spectral measurements of Nujol mulls were recorded in the region 4000–400 cm<sup>-1</sup> by using KBr plates, with Beckman IR-12 or Acculab-6 spectrophotometers or an IBM IR32 FT-IR spectrometer. <sup>1</sup>H NMR spectra were recorded at 90 MHz with a Perkin-Elmer R-32 spectrometer. Resonances were referenced internally to residual protons in the deuterated solvents. Magnetic moments were determined by the Evans method,<sup>16</sup> and X-band ESR spectra were recorded at -160 °C on dichloromethane glasses of the complexes using a Varian E-109 spectrometer. Electronic absorption spectra were recorded on dichloromethane solutions in the region 900–200 nm by using an IBM 9420 spectrophotometer.

Cyclic voltammetry experiments were performed on dichloromethane solutions containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte.  $E_{1/2}$  values (taken as  $(E_{p,a} + E_{p,c})/2$ ) were referenced to the saturated potassium chloride calomel electrode (SCE). Voltammetric measurements were taken with a Bioanalytical Systems Inc. Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035B x-y recorder. Conductivity data were obtained on ~10<sup>-3</sup> M acetonitrile solutions of complexes utilizing an Industrial Instruments Inc. Model RC-16B2 conductivity bridge.

Microanalyses were performed by Dr. H. D. Lee of the Purdue University microanalytical laboratory.

## Results and Discussion

When a mixture of the monohydrido complex [ReH(NCCH<sub>3</sub>)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> and *tert*-butyl isocyanide (ca 1:4 stoichiometric proportions) is refluxed under a N<sub>2</sub>(g) atmosphere for 30 min in 1,2-dichloroethane, the yellow solution turns a deep red-purple. Workup of this solution affords purple crystals of the 17-electron species [Re(CN-*t*-Bu)<sub>2</sub>(NCCH<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (39% yield), as well as a quantity of the analogous orange 18-electron rhenium(I) complex [Re(CN-*t*-Bu)<sub>2</sub>(NCCH<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>. The related reactions of [ReH(NCCH<sub>3</sub>)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> with isopropyl isocyanide and of the pyridine derivative [ReH(NCCH<sub>3</sub>)<sub>3</sub>(py)(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> with *tert*-butyl isocyanide and isopropyl isocyanide proceed in an analogous fashion to that described above to afford the pairs of rhenium(II) and rhenium(I) complexes [Re(CNR)<sub>2</sub>(NCCH<sub>3</sub>)<sub>2</sub>L(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>n</sub>, where R = *i*-Pr or *t*-Bu, L = CH<sub>3</sub>CN or py, and  $n = 1$  or 2.

These sets of complexes possess very similar properties, the most noteworthy features of which are described herein. The formally 17-electron species [Re(CNR)<sub>2</sub>(NCCH<sub>3</sub>)<sub>2</sub>L(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> are paramagnetic ( $\mu_{\text{eff}} = 1.2$ – $1.5 \mu_B$  for CH<sub>2</sub>Cl<sub>2</sub> solutions, by the Evans Method),<sup>17</sup> and they behave as 1:2 electrolytes in acetonitrile ( $\Lambda_M = 235$ – $276 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$  for 10<sup>-3</sup> M solutions).<sup>18</sup> They exhibit an electronic absorption band maximum between 566 and 545 nm ( $\epsilon \approx 1 \times 10^3 \text{L mol}^{-1} \text{cm}^{-1}$  for 10<sup>-4</sup> M solutions in CH<sub>2</sub>Cl<sub>2</sub>), a feature that characterizes the related spectra of other 17-electron species such as *trans*-ReCl<sub>2</sub>(CO)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> and [Re(CNAr)<sub>6</sub>]<sup>12+</sup>.<sup>19,20</sup> While a single intense  $\nu(\text{C}\equiv\text{N})$  mode between 2137 and 2100 cm<sup>-1</sup> in the Nujol mull IR spectra of these complexes is assignable to the coordinated

(16) Evans, D. F. *J. Chem. Soc.* 1959, 2003.

(17) Toluene-dichloromethane glasses (-160 °C) of these complexes did not give well-defined X-band ESR spectra except in the case of [Re(CNR)<sub>2</sub>(NCCH<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> which displayed a broad signal at  $g = 1.96$ .

(18) Geary, W. J. *Coord. Chem. Rev.* 1971, 7, 81.

(19) Hertzler, C. A.; Myers, R. E.; Brant, P.; Walton, R. A. *Inorg. Chem.* 1978, 17, 2383.

(20) Cameron, C. J.; Tetrick, S. M.; Walton, R. A. *Organometallics* 1984, 3, 240.

(14) Fanwick, P. E.; Huckaby, J. L. *Inorg. Chem.* 1982, 21, 3067.

(15) Flack, H. D. *Acta Crystallogr. Sect. A* 1977, A33, 890.

Table II. Derived Parameters for the Rigid Group Atoms of  $[\text{Re}(\text{CNCMe}_3)_2(\text{NCCH}_3)_2(\text{PPh}_3)_2](\text{BF}_4)_2 \cdot 1/2\text{CH}_2\text{Cl}_2$ 

atom	x	y	z	B, Å <sup>2</sup>	atom	x	y	z	B, Å <sup>3</sup>
CPH111	0.21477 (10)	0.2486 (4)	0.0843 (3)	3.1 (1)	CPH131	0.1796 (1)	0.5618 (4)	0.5300 (2)	3.1 (1)
CPH112	0.2432 (1)	0.2794 (4)	0.1281 (2)	4.2 (2)	CPH132	0.1551 (1)	0.5406 (4)	0.4733 (3)	4.2 (2)
CPH113	0.27079 (10)	0.2281 (5)	0.1248 (3)	5.0 (2)	CPH133	0.1563 (1)	0.4487 (5)	0.4340 (2)	5.0 (2)
CPH114	0.26986 (10)	0.1461 (5)	0.0776 (3)	4.6 (2)	CPH134	0.1819 (1)	0.3780 (4)	0.4514 (3)	5.2 (2)
CPH115	0.2414 (1)	0.1154 (4)	0.0337 (2)	4.2 (2)	CPH135	0.2064 (1)	0.3992 (4)	0.5080 (3)	4.9 (2)
CPH116	0.21384 (9)	0.1666 (5)	0.0371 (2)	3.4 (2)	CPH136	0.2052 (1)	0.4911 (5)	0.5474 (2)	4.0 (2)
CPH121	0.1841 (1)	0.3768 (5)	0.1637 (2)	3.6 (2)	CPH221	0.4249 (1)	0.5393 (5)	0.4022 (3)	4.4 (2)
CPH122	0.1726 (2)	0.4820 (5)	0.1701 (3)	5.4 (2)	CPH222	0.4158 (2)	0.4317 (5)	0.3827 (3)	5.4 (2)
CPH123	0.1744 (2)	0.5242 (4)	0.2330 (4)	7.8 (3)	CPH223	0.4210 (2)	0.3884 (5)	0.3250 (4)	7.6 (3)
CPH124	0.1876 (2)	0.4612 (6)	0.2895 (3)	7.4 (3)	CPH224	0.4354 (2)	0.4528 (6)	0.2869 (3)	7.3 (3)
CPH125	0.1991 (2)	0.3560 (6)	0.2831 (2)	6.2 (2)	CPH225	0.4446 (2)	0.5605 (6)	0.3064 (3)	7.7 (3)
CPH126	0.1973 (1)	0.3138 (4)	0.2202 (3)	4.9 (2)	CPH226	0.4393 (2)	0.6037 (4)	0.3641 (3)	5.7 (2)
CPH211	0.0838 (1)	0.0250 (4)	0.4720 (3)	3.9 (2)	CPH231	0.4518 (1)	0.3363 (5)	0.0241 (3)	4.0 (2)
CPH212	0.0554 (1)	0.0739 (6)	0.4390 (4)	5.9 (2)	CPH232	0.4490 (1)	0.2767 (5)	0.0792 (3)	4.7 (2)
CPH213	0.0549 (1)	0.1667 (6)	0.3994 (4)	7.6 (3)	CPH233	0.4754 (2)	0.2311 (6)	0.1233 (3)	6.1 (2)
CPH214	0.0827 (2)	0.2106 (5)	0.3927 (4)	6.7 (3)	CPH234	0.5047 (1)	0.2450 (6)	0.1124 (3)	6.5 (3)
CPH215	0.1112 (1)	0.1618 (6)	0.4257 (4)	6.9 (3)	CPH235	0.5075 (1)	0.3046 (6)	0.0574 (3)	6.4 (3)
CPH216	0.1117 (1)	0.0690 (6)	0.4653 (3)	5.2 (2)	CPH236	0.4810 (1)	0.3503 (5)	0.0133 (3)	5.3 (2)

## Rigid-Group Parameters

group	$x_c^a$	$y_c$	$z_c$	$\delta^b$	$\epsilon$	$\eta$
PH11	0.24232 (8)	0.1974 (3)	0.0809 (2)	2.397 (4)	2.449 (4)	0.393 (4)
PH12	0.18587 (10)	0.4190 (4)	0.2266 (2)	0.478 (5)	2.828 (4)	1.352 (4)
PH21	0.0833 (1)	0.1178 (4)	0.4323 (2)	-1.596 (4)	3.081 (4)	0.633 (4)
PH13	0.18075 (9)	0.4699 (3)	0.4907 (2)	-1.844 (4)	-2.747 (3)	2.433 (4)
PH22	0.4302 (1)	0.4961 (4)	0.3446 (2)	-0.450 (5)	2.855 (4)	1.884 (5)
PH23	0.4782 (1)	0.2907 (4)	0.0683 (2)	-0.994 (6)	2.315 (4)	-2.458 (6)

<sup>a</sup>  $x_c$ ,  $y_c$ , and  $z_c$  are the fractional coordinates of the origin of the rigid group. <sup>b</sup> The rigid-group orientation angles  $\delta$ ,  $\epsilon$ , and  $\eta$  (radians) have been defined previously: La Placa, S. J.; Ibers, J. A. *Acta Crystallogr.* 1965, 18, 511.

RNC ligands, implying that they are in a trans disposition to one another, the related  $\nu(\text{C}\equiv\text{N})$  modes of the acetonitrile ligands were not readily located and are clearly extremely weak.<sup>21</sup> Bearing in mind the all-trans geometry that characterizes the related 17-electron species  $\text{ReCl}_2(\text{CO})_2(\text{PR}_3)_2$ <sup>19,22</sup> and  $[\text{Mo}(\text{CO})_2(\text{CNR})_2(\text{PR}_3)_2]^+$ ,<sup>23</sup> we expected that such a geometry might pertain to  $[\text{Re}(\text{CNR})_2(\text{NCCH}_3)_2\text{L}(\text{PPh}_3)_2]^{2+}$ , a prediction that has been confirmed by a crystal determination on the derivative where  $\text{L} = \text{CH}_3\text{CN}$ .

The crystal that was selected for the structure determination proved to be the hemisolvate  $[\text{Re}(\text{CN}-t\text{-Bu})_2(\text{NCCH}_3)_2(\text{PPh}_3)_2](\text{BF}_4)_2 \cdot 1/2\text{CH}_2\text{Cl}_2$ . The bond distances and angles for the nongroup atoms are listed in Table V and an ORTEP drawing of the cation is shown in Figure 1. The cation and the  $[\text{BF}_4]^-$  anions were located at general positions in the unit cell and therefore possess no crystallographically imposed symmetry. The solvent was located with the carbon atom on a twofold axis so that there were only four  $\text{CH}_2\text{Cl}_2$  molecules to eight of the rhenium complex. All the bond distances and angles are typical. However, there is evidence that the six-coordinate rhenium atom is quite crowded. First, there are the angles involving the isocyanide ligands; the two  $\text{Re}-\text{C}-\text{N}$  angles are 171.5 (7)° and 174.4 (7)°, while the  $\text{C}-\text{Re}-\text{C}$  angle is 170.4 (3)°. These values can be compared to the related angles involving the coordinated nitrile ligands, viz., the  $\text{Re}-\text{N}-\text{C}$  angles are 179.0 (7) and 176.5 (7)° and the  $\text{N}-\text{Re}-\text{N}$  angle is 178.7 (2)°. Interestingly, all the  $\text{C}\equiv\text{N}$  distances are essentially equivalent. A second noteworthy feature of this structure concerns the geometry of the ligands that are trans to each other. The three phenyl rings

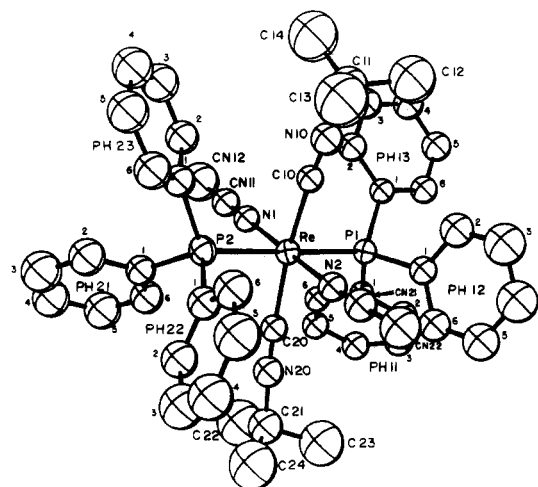


Figure 1. An ORTEP drawing of *all-trans*- $[\text{Re}(\text{CN}-t\text{-Bu})_2(\text{NCCH}_3)_2(\text{PPh}_3)_2]^{2+}$ . The ellipsoids are drawn at the 50% probability level.

on the two triphenylphosphines are in nearly an eclipsed configuration with respect to the  $\text{P}-\text{Re}-\text{P}$  axis. The three methyl groups of the *tert*-butyl isocyanide are in a similar eclipsed configuration. Since there are no strong interionic interactions that would force this configuration, it appears likely than it arises from the steric factors.

The diamagnetic 18-electron rhenium(I) congeners  $[\text{Re}(\text{CNR})_2(\text{NCCH}_3)_2\text{L}(\text{PPh}_3)_2]\text{BF}_4$ ,<sup>24</sup> which can be isolated from the same reaction mixtures that afford the rhenium(II) species, can be oxidized chemically to the dications using  $\text{AgBF}_4$  or produced from them by the zinc reduction

(21) The weakness of such modes in the IR spectra of nitrile complexes is not at all uncommon; see: Drew, M. G. B.; Tisley, D. G.; Walton, R. A. *J. Chem. Soc., Chem. Commun.* 1970, 600. Rouschias, G.; Wilkinson, G. *J. Chem. Soc. A* 1967, 993.

(22) The all-trans geometry of  $\text{ReCl}_2(\text{CO})_2(\text{PR}_3)_2$  has recently been confirmed by a single-crystal X-ray structure determination: Cotton, F. A., and co-workers, unpublished results.

(23) Conner, K. A.; Walton, R. A. *Organometallics* 1983, 2, 169.

(24) The spectroscopic properties of these diamagnetic complexes, which behave as 1:1 electrolytes in acetonitrile ( $\Lambda_M = 100\text{--}160 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$  for  $C_m \approx 10^{-3} \text{M}$ ), appear to be quite normal: IR spectra (Nujol mull)  $\nu(\text{C}\equiv\text{N})$  2244–2200 (w)  $\text{cm}^{-1}$  ( $\text{CH}_3\text{CN}$ ) and 2060–2002 (m-s or s)  $\text{cm}^{-1}$  (RNC);  $^1\text{H}$  NMR spectra (in  $\text{CD}_2\text{Cl}_2$  or  $(\text{CD}_3)_2\text{CO}$ )  $\delta$  +2.30 to +1.95 ( $\text{CH}_3\text{CN}$ ), +1.05 to +0.88 (*t*- $\text{C}_4\text{H}_9\text{NC}$ ). Further spectral details are available elsewhere; see: Allison, J. D., Ph.D. Thesis, Purdue University, 1983.

Table V. Bond Distances (Å) and Angles (deg) for [Re(CNCMe<sub>3</sub>)<sub>2</sub>(NCCH<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>·1/2CH<sub>2</sub>Cl<sub>2</sub>

Bond Distances			
Re-C10	2.023 (8)	Re-C20	2.034 (8)
Re-N1	2.058 (7)	Re-N2	2.055 (7)
Re-P1	2.454 (2)	Re-P2	2.445 (2)
C10-N10	1.15 (1)	C20-N20	1.15 (1)
N10-C11	1.50 (1)	N20-C21	1.48 (1)
C11-C12	1.53 (2)	C21-C22	1.46 (2)
C11-C13	1.53 (2)	C21-C23	1.57 (2)
C11-C14	1.50 (2)	C21-C24	1.50 (2)
N1-CN11	1.13 (1)	N2-CN21	1.14 (1)
CN11-CN12	1.47 (2)	CN21-CN22	1.46 (1)
P1-CPH111	1.824 (8)	P2-CPH211	1.833 (8)
-CPH121	1.801 (8)	-CPH221	1.824 (8)
-CPH131	1.833 (8)	-CPH231	1.822 (8)
B1-F11	1.31 (2)	B2-F21	1.27 (2)
-F12	1.27 (2)	-F22	1.20 (2)
-F13	1.31 (2)	-F23	1.36 (2)
-F14	1.32 (2)	-F24	1.38 (2)
CS-C1	1.73 (2)		

Bond Angles			
C10-Re-C20	170.4 (3)	N1-Re-N2	178.7 (2)
-N1	95.1 (3)	-P1	89.8 (2)
-N2	83.7 (3)	-P2	88.4 (2)
-P1	90.8 (2)	N2-Re-P1	90.7 (2)
-P2	88.9 (2)	-P2	91.0 (2)
C20-Re-N1	94.5 (3)	P1-Re-P2	178.18 (7)
-N2	86.8 (3)		
-P1	88.6 (2)		
-P2	92.0 (2)		
Re-C10-N10	171.5 (7)	Re-C20-N20	174.4 (7)
C10-N10-C11	176.8 (9)	C20-N20-C21	175.2 (9)
N10-C11-C12	106.8 (9)	N20-C21-C22	107 (1)
-C13	103 (1)	-C23	107 (1)
-C14	107 (1)	-C24	107 (1)
C12-C11-C13	112 (1)	C22-C21-C23	107 (1)
-C14	112 (1)	-C24	127 (1)
C13-C11-C14	115 (1)	C23-C21-C24	100 (1)
Re-N1-CN11	179.0 (7)	Re-N2-CN21	176.5 (7)
N1-CN11-CN12	179 (1)	N2-CN21-CN22	178 (1)
Re-P1-CPH111	116.8 (5)	Re-P2-CPH211	116.9 (5)
-CPH121	108.9 (5)	-CPH221	110.5 (5)
-CPH131	117.8 (5)	-CPH231	116.9 (5)
CPH111-P1-CPH121	106.0 (9)	CPH211-P2-CPH221	104.1 (9)
-CPH131	102.3 (9)	-CPH231	100.2 (9)
CPH121-P1-CPH131	103.8 (9)	CPH221-P2-CPH231	106.9 (9)
F11-B1-F12	108 (2)	F21-B2-F22	116 (2)
-F13	110 (2)	-F23	109 (2)
-F14	112 (2)	-F24	103 (2)
F12-B1-F13	109 (2)	F22-B2-F23	116 (2)
-F14	107 (2)	-F24	104 (2)
F13-B1-F14	111 (2)	F23-B2-F24	107 (2)
C1-Cs-C1	104 (2)		

of acetone solutions of [Re(CNR)<sub>2</sub>(NCCH<sub>3</sub>)L(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>. This facile reversible chemical redox behavior is reflected by the electrochemical properties of solutions of these complexes in 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH)-dichloromethane. Cyclic voltammetric measurements ( $\nu = 200\text{mV/s}$ ) show<sup>25</sup> that the species [Re(CNR)<sub>2</sub>(NCCH<sub>3</sub>)L(PPh<sub>3</sub>)<sub>2</sub>]<sup>*n*+</sup>, where L = CH<sub>3</sub>CN or py and *n* = 1 or 2, exhibit a reversible one-electron couple with an  $E_{1/2}$  value in the range +0.24 to +0.14 V vs. SCE, the actual potential depending upon the nature of L,<sup>26</sup> and a second irreversible process, corresponding to an oxidation, at  $E_{p,a} \approx +1.28$  V vs. SCE.

The preceding reactions that have been discussed involve the reactions of isocyanide ligands RNC (R = *i*-Pr or *t*-Bu) with [ReH(NCCH<sub>3</sub>)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> and [ReH-

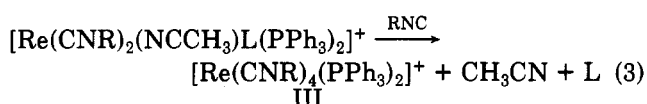
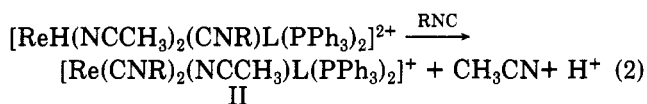
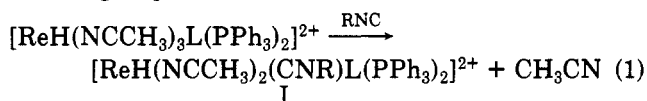
(NCCH<sub>3</sub>)<sub>3</sub>(py)(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>. Upon extending the reactions of *tert*-butyl isocyanide to include those with [ReH(NCCH<sub>3</sub>)<sub>3</sub>L(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, where L = C<sub>6</sub>H<sub>11</sub>NH<sub>2</sub> or *t*-BuNH<sub>2</sub>, we found that reaction at room temperature for 1 h in 1,2-dichloroethane gave yellow crystalline [ReH(NCCH<sub>3</sub>)<sub>2</sub>(CN-*t*-Bu)L(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>,<sup>27</sup> although in the case of L = *t*-BuNH<sub>2</sub> this complex was admixed with rather large amounts of [Re(CN-*t*-Bu)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>) (approximately a threefold quantity as estimated by cyclic voltammetry).<sup>13</sup> When these same reactions were carried for 0.5 h in refluxing 1,2-dichloroethane, the rhenium(I) salt [Re(CN-*t*-Bu)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sup>13</sup> was the preponderant product (>80% yield). This same reaction course ensued when

(25) Measurements were carried out at 22 ± 2 °C by using a Pt-bead electrode; see: Zietlow, T. C.; Klendworth, D. D.; Nimry, T.; Salmon, D. J.; Walton, R. A. *Inorg. Chem.* 1981, 20, 947 for full details of our electrochemical procedure.

(26)  $E_{1/2} = +0.14$  to  $+0.17$  V for L = py and  $+0.23$  or  $+0.24$  V for L = CH<sub>3</sub>CN.

(27) The complex [ReH(NCCH<sub>3</sub>)<sub>2</sub>(CN-*t*-Bu)(H<sub>2</sub>NC<sub>6</sub>H<sub>11</sub>)(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> was isolated in 83% yield by this procedure. Its properties resemble closely those of the seven-coordinate complexes [ReH(NCCH<sub>3</sub>)<sub>3</sub>L(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>:<sup>11</sup> IR spectrum (Nujol mull)  $\nu(\text{C}\equiv\text{N})$  2268 (sh), 2250 (m-s) cm<sup>-1</sup> (CH<sub>3</sub>CN) and 2168 (s), 2130 (sh) cm<sup>-1</sup> (*t*-BuNC); <sup>1</sup>H NMR spectrum (in (CD<sub>3</sub>)<sub>2</sub>CO)  $\delta$  -4.05 (Re-H, doublet of doublets,  $J^1(\text{P-H}) = 68$  Hz and  $J^2(\text{P-H}) = 50$  Hz); cyclic voltammogram (0.2 M TBAH-CH<sub>2</sub>Cl<sub>2</sub>)  $E_{p,a} = +1.28$  V and  $E_{p,c} = -1.83$  V vs. SCE; molar conductance,  $\Lambda_M = 266 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$  for  $C_m \approx 10^{-3}$  M.

[ReH(NCCH<sub>3</sub>)<sub>3</sub>L(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, where L = CH<sub>3</sub>CN or py, was reacted with *tert*-butyl isocyanide in refluxing ethanol for 3 h (85% yield). Thus it appears that in the reaction of RNC ligands with [ReH(NCCH<sub>3</sub>)<sub>3</sub>L(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, where L = CH<sub>3</sub>CN, py, C<sub>6</sub>H<sub>11</sub>NH<sub>2</sub>, and *t*-BuNH<sub>2</sub>, the following steps occur:



Depending upon the reaction conditions (solvent, temperature) and the nature of L, these reactions can afford products I, II, or III. This sequence of steps ((1)–(3)) was confirmed upon monitoring the reaction between [ReH(NCCH<sub>3</sub>)<sub>3</sub>(H<sub>2</sub>NC<sub>6</sub>H<sub>11</sub>)(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> and *t*-BuNC by cyclic voltammetry. By this means we obtained electrochemical evidence for the sequential formation of I, II, and III. Note that in the reactions which produce II, significant quantities of the 17-electron dicationic analogues [Re(CNR)<sub>2</sub>(NCCH<sub>3</sub>)L(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> are always produced. We believe

that this oxidation is brought about through the reaction of II with the HBF<sub>4</sub> that is released in step 2. Separate experiments (e.g., the addition of HBF<sub>4</sub> to CH<sub>2</sub>Cl<sub>2</sub> solutions of [Re(CN-*i*-Pr)<sub>2</sub>(NCCH<sub>3</sub>)py(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>) have confirmed that such an oxidation indeed occurs.

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**Registry No.** I (R = *t*-Bu, L = NH<sub>2</sub>C<sub>6</sub>H<sub>11</sub>), 91229-70-8; I (R = *t*-Bu, L = NH<sub>2</sub>-*t*-Bu), 91229-72-0; II (R = *t*-Bu, L = NCCH<sub>3</sub>), 91229-60-6; II (R = *i*-Pr, L = NCCH<sub>3</sub>), 91237-83-1; II (R = *t*-Bu, L = C<sub>6</sub>H<sub>5</sub>N), 91229-64-0; II (R = *i*-Pr, L = C<sub>6</sub>H<sub>5</sub>N), 91229-68-4; III (R = *t*-Bu), 91279-49-1; [ReH(NCCH<sub>3</sub>)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, 86664-82-6; [Re(CN-*t*-Bu)<sub>2</sub>(NCCH<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub><sup>1/2</sup>CH<sub>2</sub>Cl<sub>2</sub>, 91229-58-2; [Re(CN-*t*-Bu)<sub>2</sub>(NCCH<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, 91229-57-1; [Re(CN-*i*-Pr)<sub>2</sub>(NCCH<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, 91237-81-9; [Re(CN-*t*-Bu)<sub>2</sub>(NCCH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>N)(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, 91229-62-8; [ReH(NCCH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>N)(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, 86664-78-0; [Re(CN-*i*-Pr)<sub>2</sub>(NCCH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>N)(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, 91229-66-2; [ReH(NCCH<sub>3</sub>)<sub>3</sub>(NCCH<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, 86664-82-6; [ReH(NCCH<sub>3</sub>)<sub>3</sub>(NH<sub>2</sub>C<sub>6</sub>H<sub>11</sub>)(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, 86664-80-4; [ReH(NCCH<sub>3</sub>)<sub>3</sub>(NH<sub>2</sub>-*t*-Bu)(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, 91229-75-3; ReH<sub>5</sub>(PPh<sub>3</sub>)<sub>2</sub>(NH<sub>2</sub>-*t*-Bu), 91229-73-1.

**Supplementary Material Available:** Tables of thermal parameters for the nongroup atoms (Table III) and observed and calculated structure factors (Table IV) (40 pages). Ordering information is given on any current masthead page.

## Addition Compounds of Alkali-Metal Hydrides. 26. Facile Reaction of Borinic Esters with Lithium Monoethoxyaluminumhydride To Form Lithium Dialkylborohydrides<sup>1</sup>

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Addition of 1 mol equiv of borinic esters to lithium monoethoxyaluminumhydride in ethyl ether at 0 °C results in a facile and rapid precipitation of the dialkoxalane as a solid, producing the corresponding lithium dialkylborohydride in quantitative yield. The reaction is quite general, applicable to borinic esters of widely varied structural requirements. These derivatives are very stable and can be stored under nitrogen at 25 °C without hydride loss and either redistribution or isomerization of the alkyl groups. Methyl iodide or acids readily and quantitatively removes metal hydride from these dialkylborohydrides, generating the free dialkylboranes for further use. Thus the present study provides a simple method for preparing a wide variety of lithium dialkylborohydrides under mild conditions, valuable intermediates for storing dialkylboranes for extended periods of time, and a simple procedure for generating pure dialkylboranes as required for further application.

The utility of trialkylborohydrides as powerful selective reducing agents in organic synthesis is well-known.<sup>3</sup> Recently several routes to synthesize hindered and highly hindered trialkylborohydrides have been developed.<sup>4</sup> In contrast, very little is known about lithium borohydrides

with less than three alkyl groups on boron.<sup>5,6</sup> In large part, this deficiency can be attributed to the marked inability of dialkylboranes and the lack of general procedures for preparing them. Moreover, the synthetic routes that are well established for the synthesis of trialkylborohydrides are not applicable to the preparation of dialkylborohydrides.<sup>6,7</sup> For example, the most elegant synthesis of

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