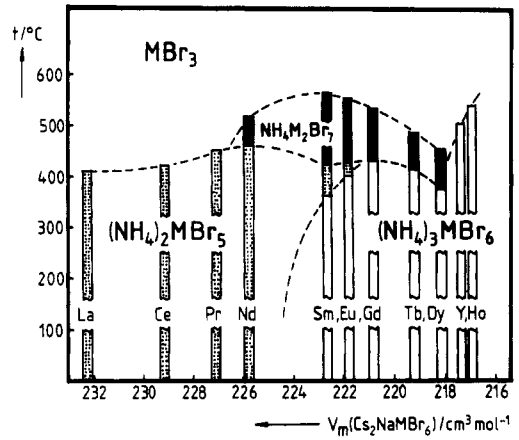


**Figure 1.** Survey of the ammonium bromide route to anhydrous rare-earth-metal bromides, $MBr_3$, showing the complex ammonium bromides stable at room temperature for M = La–Ho and their decomposition pathways as determined by Guinier–Simon X-ray patterns. Instead of the ionic radii of the trivalent rare-earth-metal cations, the molar volumes of the elpasolites $Cs_2NaMBr_6$ (see: Meyer, G.; Gaebell, H.-Chr. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1476) are used as abscissa.

chlorides must be interpreted as a two-step procedure with acid–base reaction *and* complex formation first and decomposition second.[5] This method also functions beautifully for the analogous bromides and iodides. The ammonium bromide route was particularly explored. Reaction of $NH_4Br$ and rare-earth-metal oxide, $M_2O_3$, yields $(NH_4)_2MBr_5$ for M = La–Nd, and $(NH_4)_3MBr_6$ for M = Sm–Lu. Decomposition of the latter passes through $(NH_4)_2MBr_5$ for M = Sm and Eu, and $NH_4M_2Br_7$ is observed as an intermediate for M = Nd–Dy. Figure 1 summarizes the results. The crystal structures of the halides $(NH_4)_2MX_5$ (X = Cl, Br, I) are that of $K_2PrCl_5$,[6,7] and the halides $NH_4M_2X_7$ are isotypic with $KDy_2Cl_7$ or $RbDy_2Cl_7$.[8,9]

The versatility of the ammonium halide reactions is furthermore reflected by the fact that the complex halides themselves, especially $(NH_4)_2MX_5$ and $(NH_4)_3MX_6$, are useful starting materials. For example, $(NH_4)_3YCl_6$ reacts at temperatures as low as 300–400 °C with both gases ($H_2O$, $H_2S$) or solids ($Y_2O_3$, $Y_2S_3$) to yield YOCl and YSCl, respectively. This is particularly interesting because $Y_2O_3$ does not react at these temperatures with HCl gas at all. The usual route to YOCl is the reaction of $YCl_3$ with $H_2O$, air, or $Y_2O_3$ around 500 °C. It is then obtained in the PbFCl type structure. The reaction of $(NH_4)_3YCl_6$ with $Y_2O_3$, however, provides an easy access to YOF-type[10] YOCl. Its close relationship to the novel monochloride YCl with its rich interstitial chemistry has been particularly emphasized.[11] Thermal analyses of $Y_2O_3$ and $NH_4Cl$ mixtures (1:2 molar ratio) that have recently been interpreted in terms of intermediates such as $[M(NH_3)_3]Cl_3$[12,13] are certainly misinterpreted.

Additionally, the complex ammonium halides react not only with chalcides ($Y_2O_3$, $Y_2S_3$, YSe), but also with pnictides such as YP (yielding $Y_2PCl_3$). Furthermore, alkali-metal halides like LiCl react with, for example, $(NH_4)_2EuCl_5$ to yield via the intermediate $(NH_4)_2LiEuCl_6$ the new scheelite-type[14] compound $EuLiCl_4$. Such methods seem particularly important as routes to metastable compounds or those of borderline stability. Another ternary halide that is obtained by a similar route is $KYb_2Cl_7$.[9]

It is expected that the solid-state reactions of other ammonium compounds with various metals and their compounds follow similar pathways and that their investigation will provide important insights in the production of industrially and technologically useful products.

**Acknowledgment.** Support by Deutsche Forschungsgemeinschaft, Bonn, West Germany, and Verband der Chemischen Industrie, Frankfurt, West Germany, is gratefully acknowledged.

**Registry No.** $NH_4Cl$, 12125-02-9; $NH_4Br$, 12124-97-9; $NH_4I$, 12027-06-4; Li, 7439-93-2; Zn, 7440-66-6; La, 7439-91-0; Y, 7440-65-5; Cu, 7440-50-8; $UH_3$, 13598-56-6; $NH_4ReO_4$, 13598-65-7; $Li_3N$, 26134-62-3; $LiYO_2$, 12169-03-8; $Y_2O_3$, 1314-36-9; $Y_2S_3$, 12039-19-9; YP, 12294-01-8; $(NH_4)_3YCl_6$, 59230-45-4; $(NH_4)_3YBr_6$, 98218-63-4; $(NH_4)_3YI_6$, 98218-64-5; $(NH_4)_2EuCl_5$, 97253-02-6; $(NH_4)_2LiEuCl_6$, 98218-65-6; $(NH_4)_2UCl_6$, 22949-76-4; $NH_4Y_2Cl_7$, 84556-33-2; $(NH_4)_3SmBr_6$, 98218-66-7; $(NH_4)_2SmBr_5$, 98244-73-6; $NH_4Sm_2Br_7$, 98218-67-8; $H_2O$, 7732-18-5; $H_2S$, 7783-06-4; LiCl, 7447-41-8; $NH_3$, 7664-41-7; $(NH_4)_2ZnCl_4$, 14639-97-5; $(NH_4)_2LaCl_5$, 78476-14-9; $(NH_4)_2CuCl_3$, 61288-98-0; Re, 7440-15-5; $N_2$, 7727-37-9; HCl, 7647-01-0; $H_2$, 1333-74-0; $(NH_4)_2LiYCl_6$, 98218-68-9; $PH_3$, 7803-51-2; YOBr, 15923-89-4; YOI, 66923-06-6; YOCl, 13759-29-0; YSCl, 98218-69-0; $LiEuCl_4$, 98218-70-3; $UCl_4$, 10026-10-5; $YCl_3$, 10361-92-9; $SmBr_3$, 13759-87-0.

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## Configurational Processes in Coordinated Ligands. Extremely Facile Phosphorus Inversion in the Pyramidal Terminal Phosphide Complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PRR')$

*Sir:*

Although configurational processes at coordinated sulfur and selenium have been studied extensively,[1] little is known regarding inversion barriers at coordinated phosphorus.[2,3] Complexes with terminal pyramidal phosphide ligands have been of considerable recent interest,[4] and in a brief note Malisch has indicated that $(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)(P(i\text{-}Pr)_2)$ has a phosphide phosphorus inversion barrier of 14.4 kcal/mol.[2] We have become interested in the structure and reactivity of chiral pyramidal phosphide complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PRR')$,[5] and we report here their dynamic NMR behavior and configurational stability at rhenium. These data establish inversion barriers that are among

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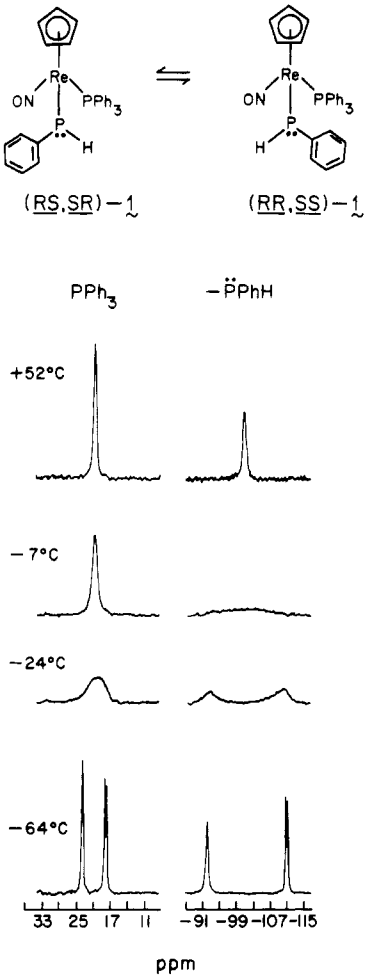


**Figure 1.** Variable-temperature $^{31}P\{^1H\}$ NMR spectra of **1** in THF.

the lowest yet observed for trivalent phosphorus.[6]

The phosphide complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PRR')$ were prepared in 80–92% yields by the sequential reaction of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OSO_2\text{-}p\text{-}C_6H_4CH_3)$ with PRR'H and then O-*t*-$Bu^-K^+$.[5,7] The phenylphosphide complex $(\eta^5\text{-}C_5H_5)$-Re(NO)($PPh_3$)(PPhH) (**1**) was studied first. Low-temperature $^{31}P\{^1H\}$ NMR spectra of **1** showed two $PPh_3$ and two PPhH resonances (Figure 1), corresponding to two isomers. These isomers interconverted, for at higher temperatures both sets of resonances broadened, coalesced, and resharpened as shown in Figure 1. Similarly, the −74 °C $^1H$ NMR spectrum of **1** (THF-$d_8$) contained two $\eta^5\text{-}C_5H_5$ ($\delta$ 5.19, 4.85) and two PH ($\delta$ 3.74 (br dd, $^1J_{PH}$ = 209 Hz), 3.34 (br d, $^1J_{PH}$ = 199 Hz)) resonances of equal intensity, which coalesced to a single set of resonances at higher temperatures. From the $\eta^5\text{-}C_5H_5$ resonances, $\Delta G^{\ddagger}_{243}$ = 11.5 ± 0.1 kcal/mol was calculated.[8] The KBr IR spectrum of complex **1** also exhibited two well-separated $\nu_{N\equiv O}$ (1654, 1627 $cm^{-1}$ (vs)) and $\nu_{P-H}$ (2281, 2255 $cm^{-1}$ (m)) absorbances. We considered it highly probable that the two isomers were the diastereomers (*RS,SR*)-**1** and (*RR,SS*)-**1**. However, from the above data the possibility that the isomers were two Re–PPhH rotamers of a single diastereomer of **1** could not be rigorously excluded.

Accordingly, we prepared the phosphide complex $(\eta^5\text{-}C_5H_5)$-Re(NO)($PPh_3$)($P(p\text{-}C_6H_4CH_3)_2$) (**2**, Figure 2),[7] in which the diastereotopic $p\text{-}C_6H_4CH_3$ groups could not be exchanged by a

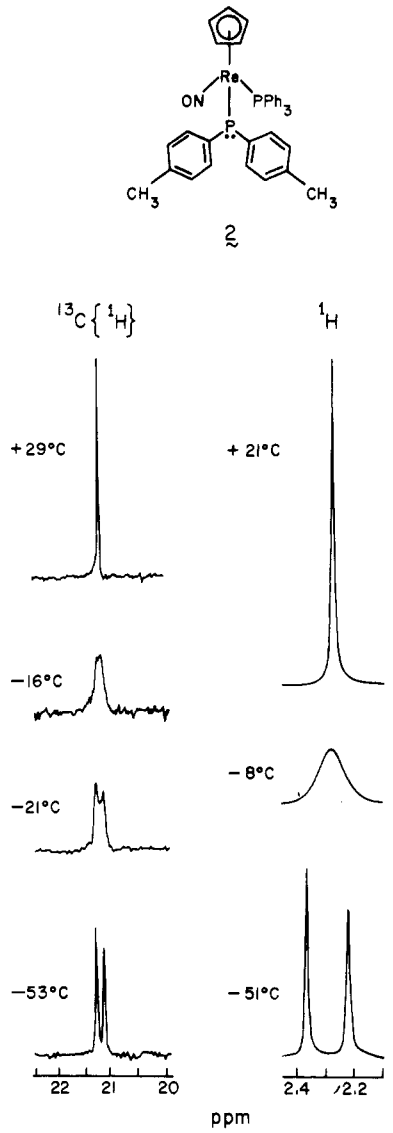


**Figure 2.** Variable-temperature $^{13}C\{^1H\}$ and $^1H$ NMR spectra of the $CH_3$ groups of **2** in THF-$d_8$.

rotational process. Although the $^{31}P\{^1H\}$ NMR spectrum of **2** (THF-$d_8$, −32 °C: 19.23 (d, $J_{PP}$ = 15.3 Hz), −50.98 (d, $J_{PP}$ = 15.3 Hz) ppm) was essentially temperature independent (−62 to +50 °C), the $^1H$ and $^{13}C\{^1H\}$ NMR spectra showed a dynamic process that equivalenced the $p\text{-}C_6H_4CH_3$ groups. From the $CH_3$ resonances of the $^1H$ NMR spectra (Figure 2), $\Delta G^{\ddagger}_{264}$ = 13.0 ± 0.1 kcal/mol was calculated.[8] Hence, isomerization of **2** (and, by extrapolation, **1**) requires an inversion of configuration.

In principle, the inversion of configuration could involve either the phosphorus or rhenium atoms. Hence, optically active **2** ($[\alpha]^{25}_{546}$ = 397°, *c* 0.000 73 g/mL, THF, 25 °C) was prepared from (−)-(*S*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OSO_2\text{-}p\text{-}C_6H_4CH_3)$,[9] and it was found to be configurationally stable (3 h, <2% racemization). This excluded rhenium inversion. Furthermore, processes involving prior phosphide or $PPh_3$ ligand dissociation were eliminated because coupling constants $^2J_{PP}$ were retained in $^{31}P\{^1H\}$ NMR spectra of **2** at temperatures as high as 50 °C ($\Delta G^{\ddagger}_{dissoc}$ > 17 kcal/mol).

Phosphorus inversion barriers for trialkylphosphines are typically >30 kcal/mol.[6] Previously, low phosphorus inversion barriers have been observed in silylphosphines such as $(C_6H_5)P(SiH(CH_3)_2)_2$ (12 kcal/mol), acylphosphines such as $(C_6H_5)P(COCH(CH_3)_2)_2$ (12 kcal/mol), and substituted phospholes (15–16 kcal/mol).[6a] Like the former example, phosphides **1** and **2** both have an

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electropositive substituent. Furthermore, the X-ray crystal structure of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PPh_2)$ shows the phosphide phosphorus to be considerably closer to planarity (sum of bond angles 323°) than that of $PPh_3$ (sum of bond angles 309°).[5] Finally, there exist a number of ways to delocalize the phosphide lone pair in **1** and **2** to rhenium ($\eta^5$-$C_5H_5$ slippage, NO bending, direct interaction with an unoccupied orbital), any of which would contribute to a lowering of the inversion barrier. Further studies of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)$ complexes of this interesting[4] and increasingly useful[10] ligand type are in progress.

**Acknowledgment.** We thank the National Science Foundation for support of this research. The 300-MHz NMR spectrometer utilized in this study was acquired via NSF and DOD instrumentation grants.

**Supplementary Material Available:** Table of microanalytical, IR, and NMR ($^1H$, $^{13}C$, $^{31}P$) data for the new compounds (6 pages). Ordering information is given on any current masthead page.

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## Synthesis, Spectroscopy, and Reactivity of Bis[(cyclooctadiene)(μ-hydroxypyridinato)iridium(I)]. A System Containing Two Interacting $d^8$ Metal Centers Capable of Formal Four-Electron Oxidations

*Sir:*

We have renewed our interest in the study of binuclear metal complexes with the weakly interacting $d^8$–$d^8$ electronic configuration,[1] because these systems may be capable of participating in multielectron photochemical processes. We now wish to report the synthesis, characterization, and reaction chemistry of a new series of binuclear, ligand-bridged, square-planar Ir(I) complexes that incorporate many of the factors we believe are needed to achieve excited-state multielectron transfers. The new complexes are of the general form $[Ir(COD)(\mu\text{-}L)]_2$ where L is either of the well-documented bridging ligands[2] 2-hydroxypyridinate (hp) or 6-methyl-2-hydroxypyridinate (mhp). The $[Ir(COD)(\mu\text{-}L)]_2$ compounds are synthesized in high chemical yields via the addition of stoichiometric amounts of NaL to THF solutions of $[Ir(COD)Cl]_2$.[3,4] The compounds are orange-red, slightly air-sensitive substances that are easily crystallized to yield X-ray quality crystals.

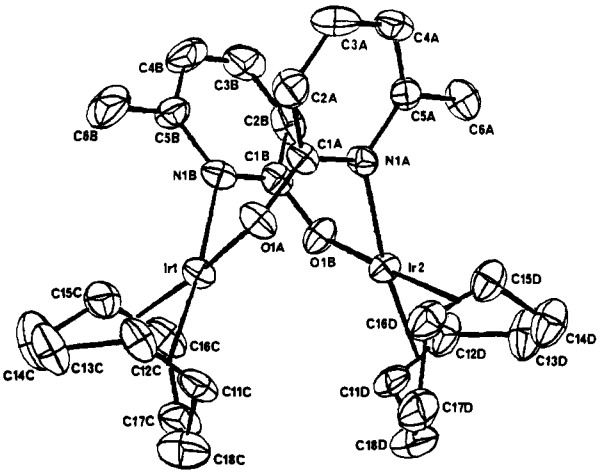


**Figure 1.** ORTEP drawing of $[Ir(COD)(\mu\text{-}mhp)]_2$ showing the atomic numbering scheme. Thermal ellipsoids are at the 50% probability level.

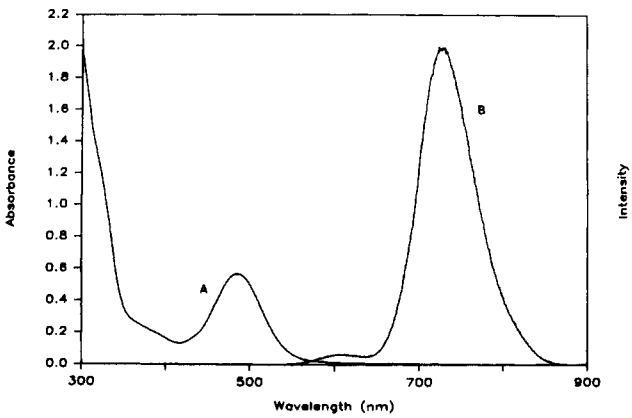


**Figure 2.** Room-temperature absorption spectrum (curve A) and 77 K emission spectrum (curve B) of $[Ir(COD)(\mu\text{-}mhp)]_2$. The emission spectrum is uncorrected for photomultiplier tube response.

The X-ray structural determination of the L = mhp compound[5-7] verifies the binuclear nature of these compounds and illustrates several of their novel features. An ORTEP view is shown in Figure 1. The coordination sphere at each Ir(I) center is made up of a chelating $\eta^4$-COD ligand, a pyridine nitrogen from one and a pyridinolate oxygen from the other bridging mhp group. The eight-membered $(IrNCO)_2$ ring adopts a distorted "tub" conformation that gives an Ir(I)–Ir(I) distance of 3.242 (1) Å. This distance is indicative of a significant Ir(I)–Ir(I) interaction and is similar to that found in $[Ir(COD)(\mu\text{-}pz)]_2$ (3.216 (1) Å), which contains a $(IrNN)_2$ six-membered ring in a "boat" conformation. The relative orientation of the two Ir(I) square planes in the mhp-bridged compound is significantly different from either the "face to face" geometry common for $d^8$–$d^8$ complexes containing four bridging ligands, i.e. $Rh_2L_4^{2+}$ (L = bridging diisocyanide ligand),[8] or the "open book" orientation found in the

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(3) Characterization of $[Ir(COD)(\mu\text{-}mhp)]_2$: $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C) mhp ring δ 7.022 (t, 1 H, *p*-H), 6.162 (t, 2 H, *m*-H), and 2.802 (s, 3 H, $CH_3$), COD olefinic δ 4.653 (m, 1 H), 4.255 (m, 1 H), 3.728 (m, 1 H), and 2.614 (m, 1 H), COD methylene δ 2.76 (m, 1 H), 2.48 (m, 2 H), 2.76 (m, 1 H, COD methylene), 2.10 (m, 1 H), 1.69 (m, 2 H), 1.41 (m, 1 H), and 1.26 (m, 1 H); $\lambda_{max}$ = 484 nm, $\epsilon_{max} = 4.6 \times 10^3$ $M^{-1}$ $cm^{-1}$. Anal. Calcd for $Ir_2C_{28}H_{36}N_2O_2$: C, 41.16; H, 4.44; N, 3.43. Found: C, 41.13; H, 4.70; N, 3.56.
(4) Characterization of $[Ir(COD)(\mu\text{-}hp)]_2$: $^1H$ NMR (300 MHz, $C_6D_6$) hp ring δ 8.000 (m, 1 H, *o*-H), 6.595 (m, 1 H, *p*-H), 6.426 (m, 1 H, *m*-H), and 5.872 (m, 1 H, *m*-H); COD olefinic δ 5.162 (m, 1 H), 4.709 (m, 1 H), 3.910 (m, 1 H), and 3.012 (m, 1 H), COD methylene δ 2.908 (m, 1 H), 2.54 (m, 2 H), 2.02 (m, 1 H), 1.82 (m, 2 H), 1.39 (m, 1 H), and 1.26 (m, 1 H); $\lambda_{max}$ = 490 nm, $\epsilon_{max} = 4.7 \times 10^3$ $M^{-1}$ $cm^{-1}$. Anal. Calcd for $Ir_2C_{26}H_{32}N_2O_2$: C, 39.58; H, 4.09; N, 3.55. Found: C, 39.87; H, 4.38; N, 3.63.
(5) $^1H$ NMR spectra of the mhp and hp compounds are consistent with the X-ray crystal structure analysis of the mhp compound.
(6) Crystallographic data for $[Ir(COD)(\mu\text{-}mhp)]_2$: $M_r$ = 817.04; monoclinic; space group $P2_1/c$; $a$ = 14.847 (5) Å, $b$ = 11.991 (2) Å, $c$ = 14.661 (11) Å; $\alpha$ = 90.04 (4)°, $\beta$ = 104.99 (4)°, $\gamma$ = 89.99 (2)°; $V$ = 2521 Å$^3$; $Z$ = 4; $\rho$(calcd) = 2.15 g cm$^{-3}$; crystal dimensions 0.15 × 0.2 × 0.2 mm; Mo Kα radiation, λ = 0.71073 Å; Enraf-Nonius SPD-CAD4 diffractometer; $R$ = 0.0295, $R_w$ = 0.0313 for 3335 observed reflections with $F_0^2 > \sigma(R_0^2)$. An empirical absorption correction was applied. All calculations were carried out on PDP 8A and 11/34 computers using the Enraf-Nonius CAD 4-SDP programs as described previously: Bohling, D. B.; Gill, T. P.; Mann, K. R. *Inorg. Chem.* **1981**, *20*, 194.
(7) Positional parameters are available as supplementary material. The full details of the structures of $[Ir(COD)(\mu\text{-}mhp)]_2$ and $[Ir(COD)(hp)Cl_2]$ will be described elsewhere.
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