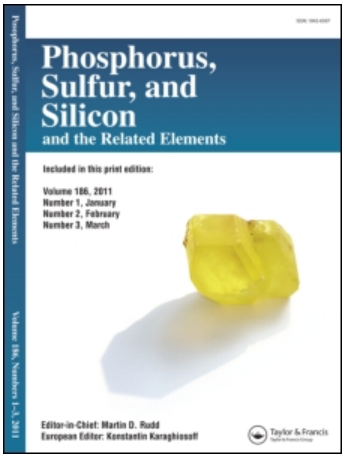

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Phosphorus-Nitrogen Compounds as Complex Ligands

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PHOSPHORUS-NITROGEN COMPOUNDS AS COMPLEX LIGANDS

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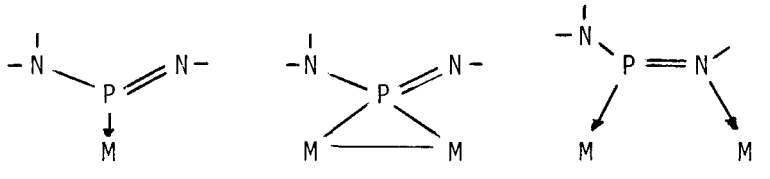
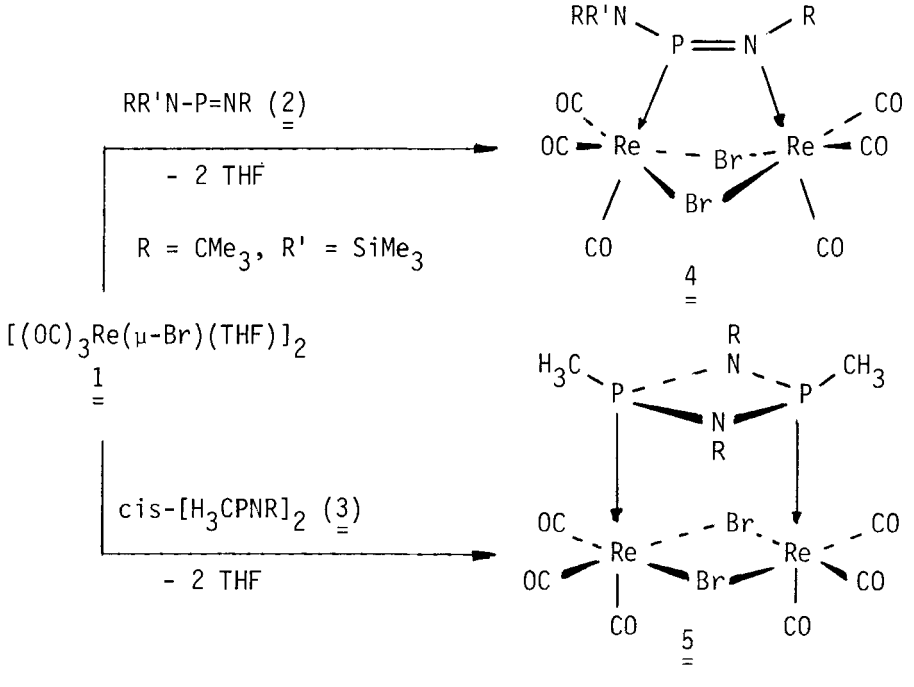
Amino(imino)phosphanes(σ^2-phosphazenes) of the type -N-P=N- are useful complex ligands.

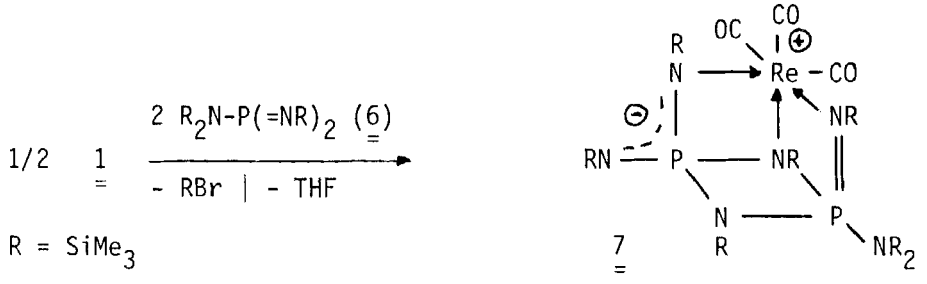


Until now only P-coordination (A) [1] and (B) [2] have been observed.



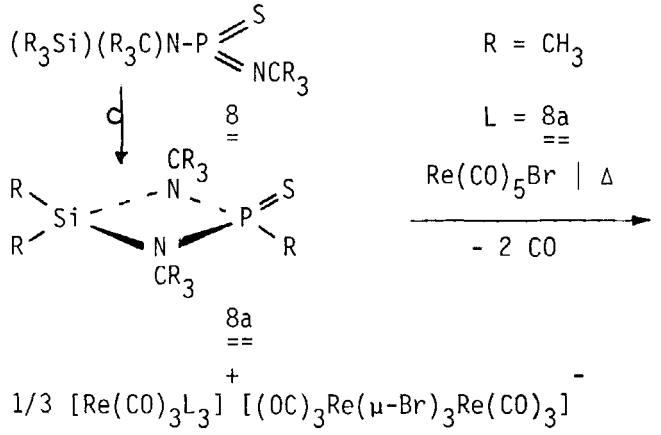
Starting with $[(OC)_3Re(\mu\text{-}Br)(THF)]_2$ (1) and RR'N-P=NR (2), R = CMe_3, R' = $SiMe_3$, complex 4 with the coordination type (C) has been synthesized. 1 and cis-$[RPNCR_3]_2$ (3), R = CH_3, afford 5.

A further variant of the synthesis potential of 1 is the tricyclic rhenium-carbonyl complex 7 [3] with incorporated $P(NSiMe_3)_3^-$, a derivative of the monomeric metaphosphate PO_3^-.



The ligand properties of the σ^3-phosphazenes 6 and RR'N-P(S) = NR (8), R = CMe_3, R' = $SiMe_3$, are even more variable.

In the first step of the reaction of 8 with $Re(CO)_5Br$ isomerization to the diazaphosphasiletidine 8a occurs [4].



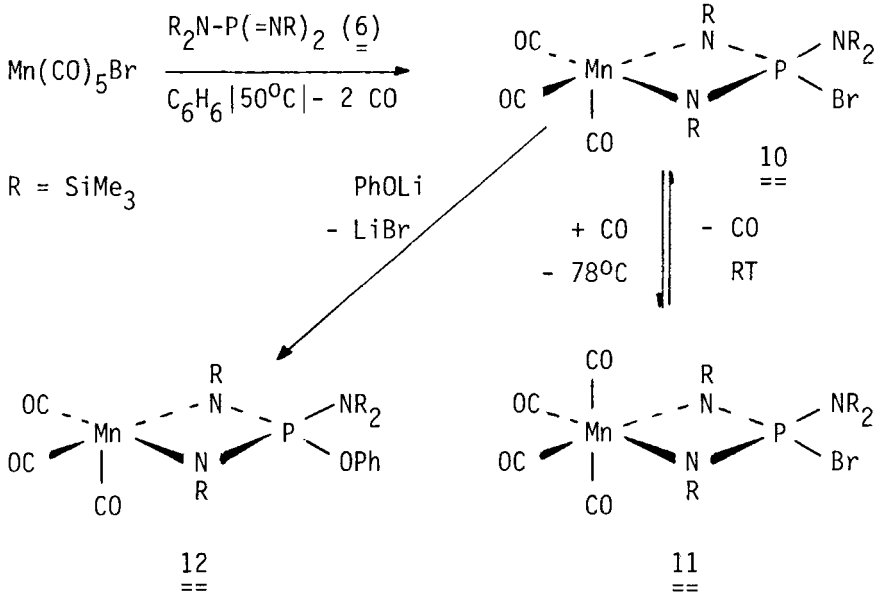
$$1/3\ [Re(CO)_3L_3]^+\ [(OC)_3Re(\mu\text{-}Br)_3Re(CO)_3]^-$$

9

The reaction sequence for the formation of 9 is:
cis-$(OC)_4ReBr(L)$ ⟶ trans-$[(OC)_3Re(\mu\text{-}Br)(L)]_2$ ⟶ 9 (L = 8a with P=S→coordination).

From 6 and $Mn(CO)_5Br$ the 16-electron manganese(I) complexes 10 and 12 can be synthesized according to Scheme 1.

Scheme 1



All compounds have been characterized NMR-spectroscopically. 10 and 12 show dynamic behaviour. The structures of 4, 7, 9 and 12 have been confirmed by X-ray structure analysis. The metal geometry of the 16 electron manganese(I) complex 12 is distorted square pyramidal.

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3. O. J. Scherer, J. Kerth and M. L. Ziegler, Angew. Chem., 95, 510 (1983); Angew. Chem. Int. Ed. Engl., 22, 503 (1983).

4. O. J. Scherer and J. Kerth, J. Organomet. Chem., 243, C 33 (1983). For 9 we erroneously proposed the dinuclear structure $[(OC)_3ReBr(R(S)P(NCR_3)SiR_2NCR_3)]_2$, R = CH_3.