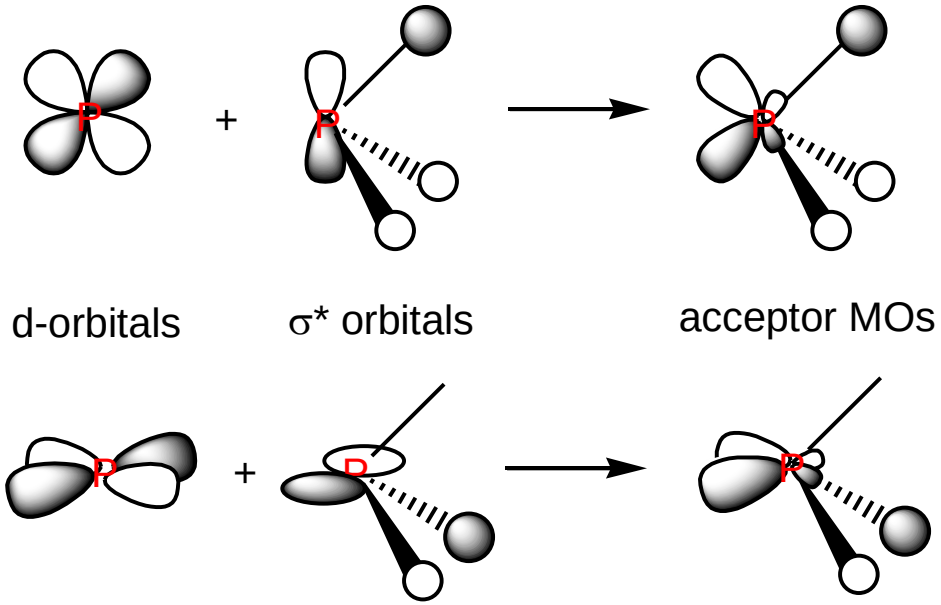
Phosphines

:PR_3 - very important ligands

- σ-donors
- π-acceptors

• For years, it was assumed that π-backdonation occurred from the metal into empty d-orbitals on phosphorus.

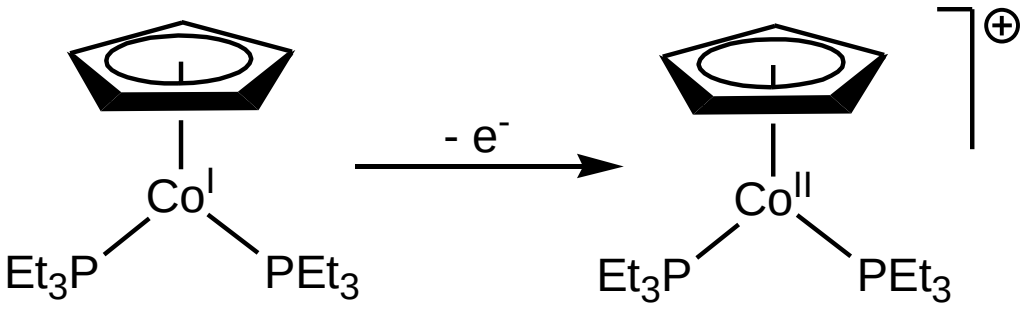
• Actually: π-backdonation occurs into MOs formed by combination of two d-orbitals on phosphorus and the σ^* orbitals involved in P-R bonding.



•Each acceptor MO has 2 lobes (similar to a d-orbital) but is antibonding with respect to the P-R bond

•As the amount of π-backdonation increases, the length of P-R increases. This can be observed in the crystal structures of phosphine complexes

Phosphines

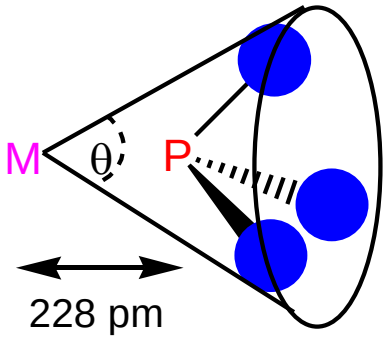


Average Co-P	221.8 pm	223.0 pm
Average P-C	184.6 pm	182.9 pm

• A huge variety of phosphines have been prepared, many of which are commercially available. One can just choose a phosphine with the desired steric (size) and electronic properties (σ-donation/π-acceptance).

Phosphines

• The size of ligands (not just phosphines) can be measured using the concept of a cone angle (Chadwick A. Tolman, *Chem. Rev.*, **1977**, 313).



- TM-P distance fixed at 228 pm to standardize the cone angle (θ).
- The cone encompasses the van der Waals radii of the outermost atoms of the ligand.

Cone angles measured by crystallography (although TM-P bond distance fixed at 228 pm)

• Electronic properties measured by IR and electrochemistry – ν(CO) and $E_{1/2}$ for oxidation or reduction measured for a large series of carbonyl phosphine complexes with different PR_3 (*e.g.* $[Ni(CO)_3(PR_3)]$ or $[CpFeMe(CO)(PR_3)]$) [ϕ = old fashioned abbreviation for phenyl]

Phosphines

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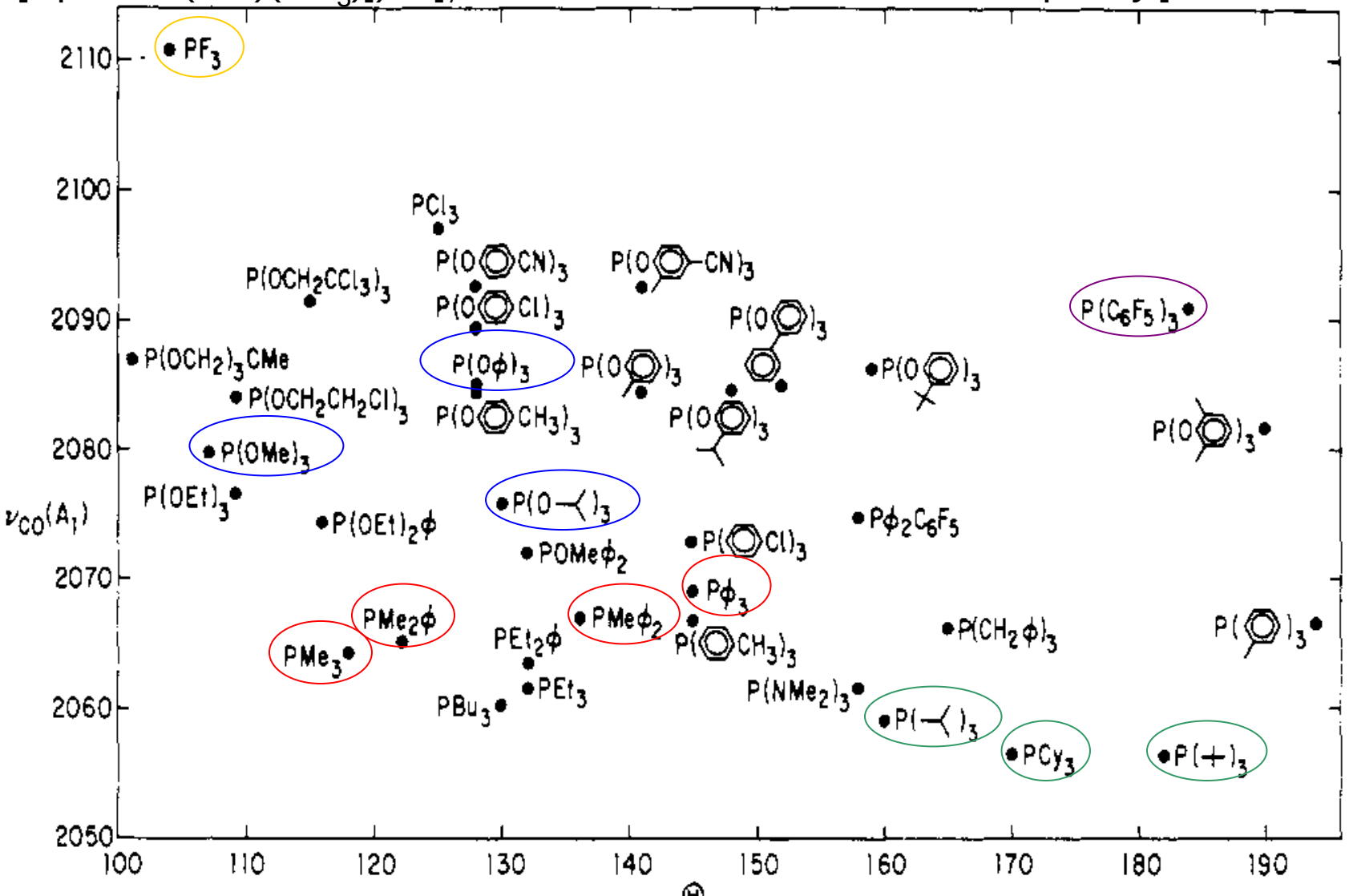
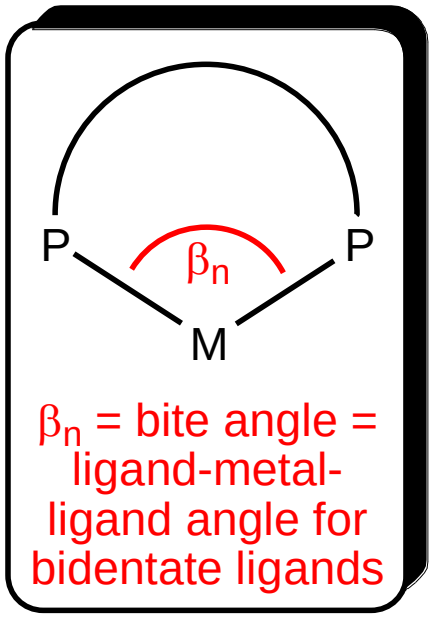
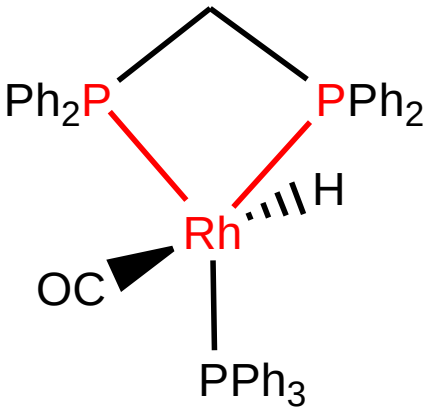


Bite angles for bidentate ligands



β_n = bite angle = ligand-metal-ligand angle for bidentate ligands

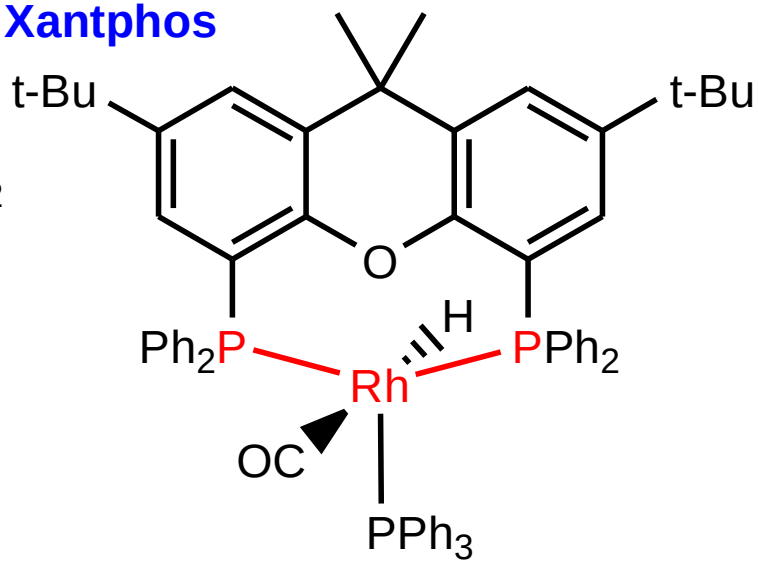
DPPM



β = 72 ^{o}

small bite angle

Xantphos



β = 111 ^{o} = large bite angle

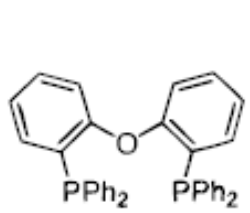
Bite angle can have a profound effect on the rate and selectivity of metal catalyzed reactions

Bite angles for bidentate ligands

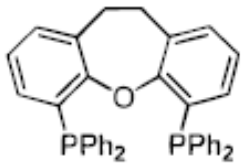
Table 6. Results of the Hydroformylation of 1-Octene at 80 °C Using Xantphos Ligands (11)[a]

ligand	β_n[b] (deg)	*l*:*b* ratio[c]	linear aldehyde[c] (%)	isomer[c] (%)	TOF[c,d]	ratio ee:ae
11b	102	8.5	88.2	1.4	36.9	3:7
11c	108	14.6	89.7	4.2	74.2	7:3
11d	108	34.6	94.3	3.0	81.0	6:4
11e	110	50.0	93.2	4.9	110	7:3
11f	111	52.2	94.5	3.6	187	7:3
11g	113	49.8	94.3	3.8	162	8:2
11h	114	50.6	94.3	3.9	154	7:3
11i	114	69.4	94.9	3.7	160	8:2
11j	120.6	50.2	96.5	1.6	343	6:4

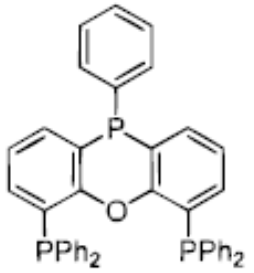
Bite angles for bidentate ligands



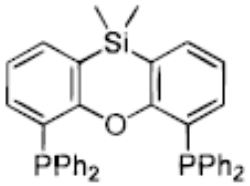
11a, DPEphos



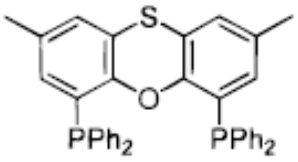
11b, Homoxantphos



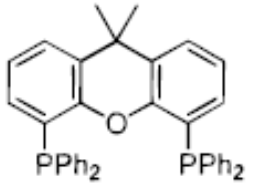
11c, Phosxantphos



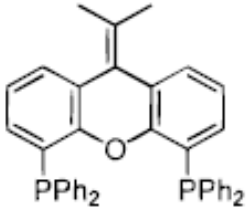
11d, Sixantphos



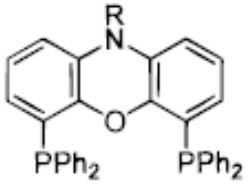
11e, Thixantphos



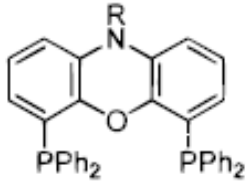
11f, Xantphos



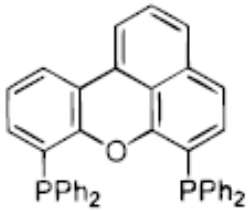
11g, Isopropxantphos



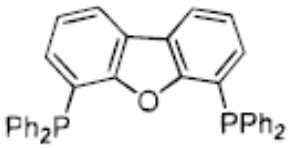
11h, R = Bn, Benzylnixantphos



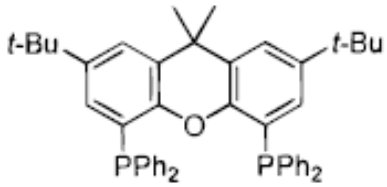
11i, R = H, Nixantphos



11j, Benzoxantphos



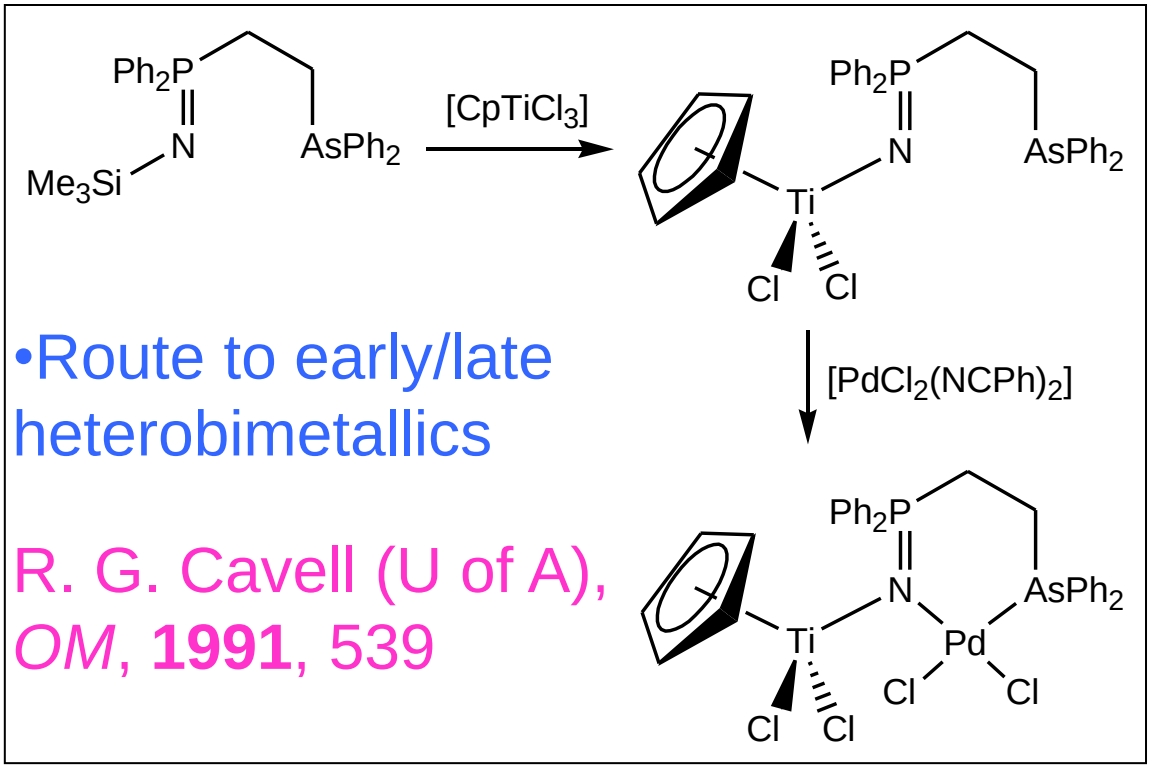
11k, DBFphos



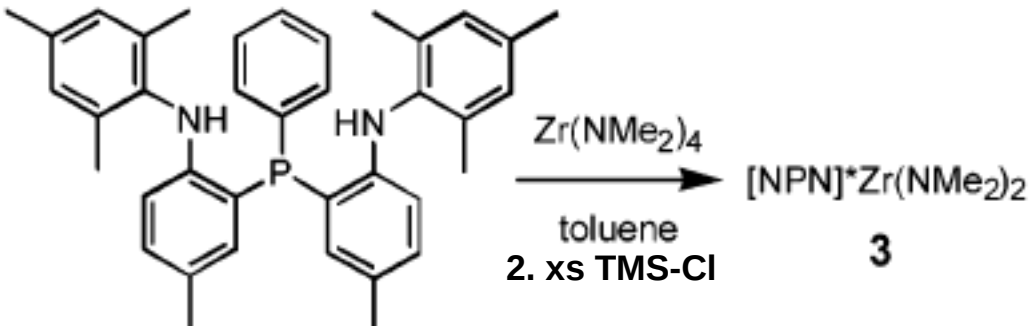
11l, *t*-Bu-xantphos

Phosphines/Arsines in early TM and lanthanide chemistry

- **PR_3 excellent ligands for soft late transition metals**
- **PR_3 typically NOT v. suitable to form complexes with hard early TMs (PR_3 > PAr_3)**
- **AsR_3 even worse, and early TM SbR_3 or BiR_3 complexes unknown**
- **NPh_3 useless as a ligand for early or late TMs (terrible donor), NMe_3 OK for early TMs**

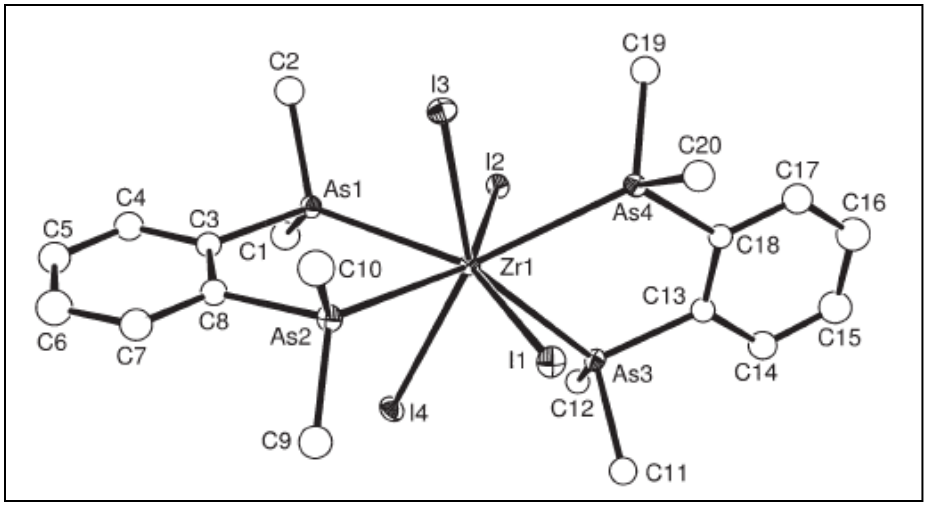


Phosphines/Arsines in early TM and lanthanide chemistry



•Hard/Soft donor combination

M. D. Fryzuk (UBC), *OM*, **2005**, 1112



•Rare early TM (Ti, Zr, Hf) arsine complexes

G. Reid (U Southampton), *DT*, **2004**, 3005 & EJIC, **2001**, 2927