Anorganische Strukturen und Reaktionsmechanismen

CHE.367

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Literatur

- J. Huheey, E. Keiter, R. Keiter: *Anorganische Chemie*
- R.H. Crabtree: *The Organometallic Chemistry of the Transition Metals*
- J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke: *Principles and Applications of Organotransition Metal Chemistry*
- J. Hartwig: *Organotransition Metal Chemistry*

Übersicht

- Struktur und Bindung von Komplexen
- Dative Liganden

  CO

  Phosphane und ähnliche

  Carbene

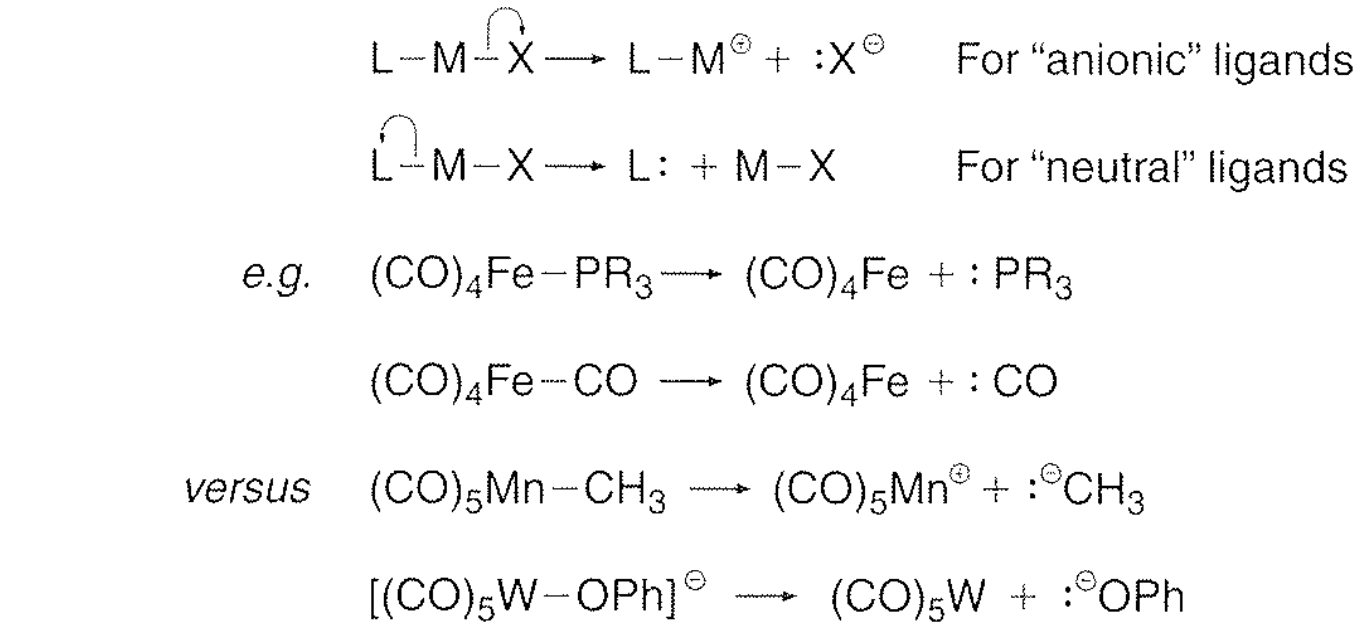
  Carbine

  Olefine, Alkine, Arene

  Neutrale N, O, S Liganden

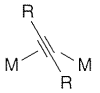
  σ-Komplexe: H_2, R_3SiH, Alkane

Anionische und neutrale Liganden

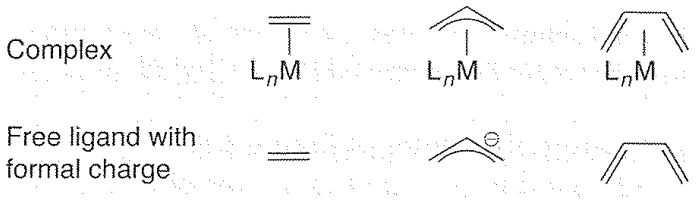


Struktur und Bindung

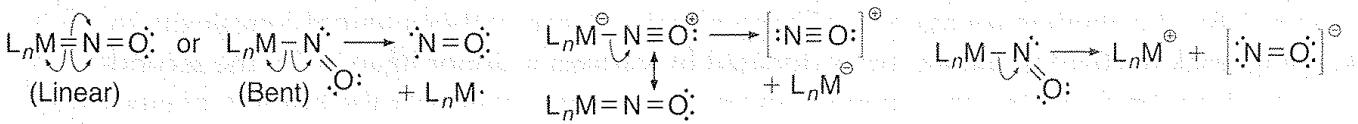
Ligand	Formal charge	Electrons donated: Ionic model	Electrons donated: Covalent model	Bonding mode
$H^{\ominus}$	−1	2	1	η^2
Halide (terminal)	−1	2	1	η^1
Halide (bridging)	−1	4	3	μ^2
Akyl, aryl, vinyl, alkynyl, silyl, germyl, stannyl, alkoxo, amido, thiolato, or phosphido	−1	2	1	
	−1	2	1	μ^2
	0	2	2	μ^2
	−1	4	3	η^2
	−1	4	3	μ^2, η^2
	−1	4	3	η^3
	0	4	4	η^4
	−1	6	5	η^5
	0	6	6	η^6

Ligand	Formal charge	Electrons donated: Ionic model	Electrons donated: Covalent model	Bonding mode
	−1	2	1	η^1
	−1	4	3	η^2
	0	2	2	η^2
	0	2	2	η^1
	0	2 or 4	2 or 4	η^2
	0	4	4	η^2, η^2
	0	2	2	
	−2	4	2	
	−2	4	2	μ^2
M=O M=NR	−2	4 or 6	2 or 4	
	−1	2	1	
M−N≡O	+1	2	3	

Struktur und Bindung



Even-electron π-systems are considered to be neutral ligands and odd-electron π-systems are considered to be charged ligands or odd-electron donors.



Covalent model | Ionic model (Linear) | Ionic model (Bent)

Linear and bent nitrosyl ligands.

Oxidationsstufe und Elektronenanzahl

EXAMPLE

$$CpFe(CO)_2(C_2H_5)$$

By the neutral system, this complex contains

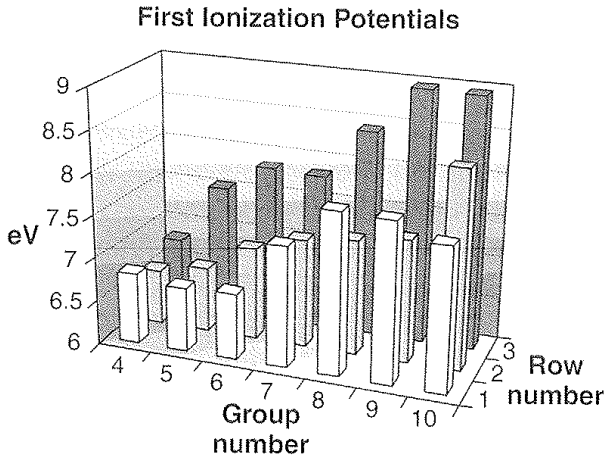
1. A metal from group 8
2. Two two-electron CO ligands
3. A five-electron Cp ligand
4. A one-electron C_2H_5 (ethyl) ligand

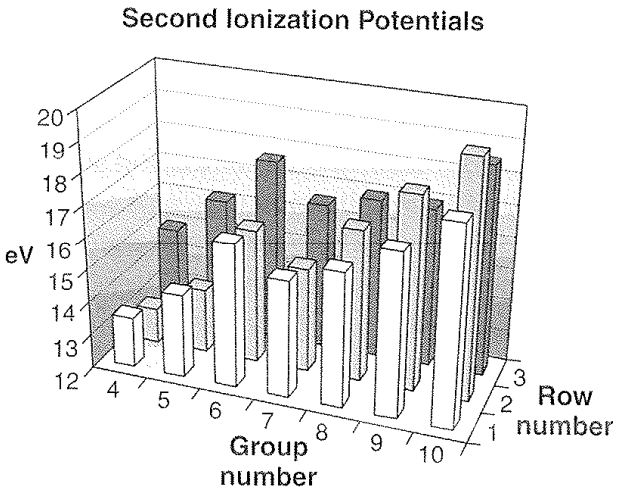
The total number of electrons is then $8 + (2 \times 2) + 5 + 1 = 18$.

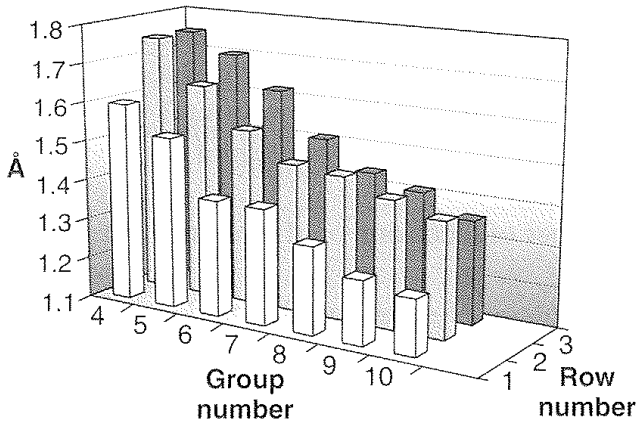
By the charged system, one can determine the total number of electrons in $CpFe(CO)_2(C_2H_5)$ by the following system:

1. This complex contains the following types of ligands:
   - Two CO ligands: Neutral, two electrons each = four electrons
   - Cp: Anionic, six-electron donor
   - C_2H_5: Anionic, two-electron donor
   - Total: 2− charge, 12 electrons donated
2. Oxidation state: The complex is neutral overall and possesses two anionic ligands. The metal, therefore, has an oxidation state of 2+.
3. *d*-Electron count: Iron is in group 8. With a 2+ charge, the metal is d^6.
4. Total number of electrons: 12 electrons from the ligands + six *d*-electrons = 18 total electrons.

Trends der Metalle





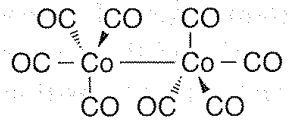


Trends in covalent radii for the transition metals. Data from Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. *J. Chem. Soc., Dalton Trans.* **2008**, 2832.

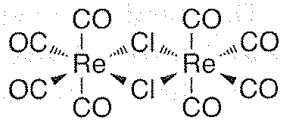
Mehrkernige Komplexe und M-M Bindung

$$\text{Number of M–M bonds} = \frac{18 \cdot M - N}{2}$$

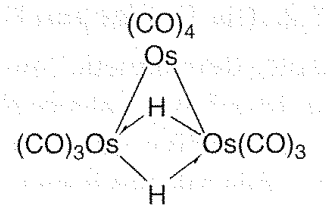
M = number of metals
N = total number of valence electrons



$$\frac{18 \cdot 2 - 34}{2} = 1$$



$$\frac{18 \cdot 2 - 36}{2} = 0$$



Neutral, half-arrow method:
$[18 \cdot 3 - (3 \cdot 8) - (10 \cdot 2) - (2 \cdot 3)]/2$
$= [54 - 24 - 20 - 6]/2$
$= 4/2 = 2$ M–M bonds

Mehrkernige Komplexe und M-M Bindung

$$\text{Number of M–M bonds} = \frac{18 \cdot M - N}{2}$$

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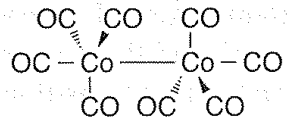
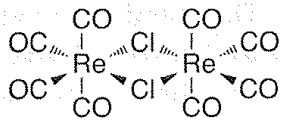


$$\frac{18 \cdot 2 - 34}{2} = 1$$



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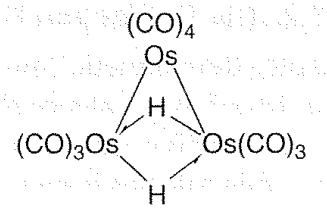

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$[18 \cdot 3 - (3 \cdot 8) - (10 \cdot 2) - (2 \cdot 3)]/2$
$= [54 - 24 - 20 - 6]/2$
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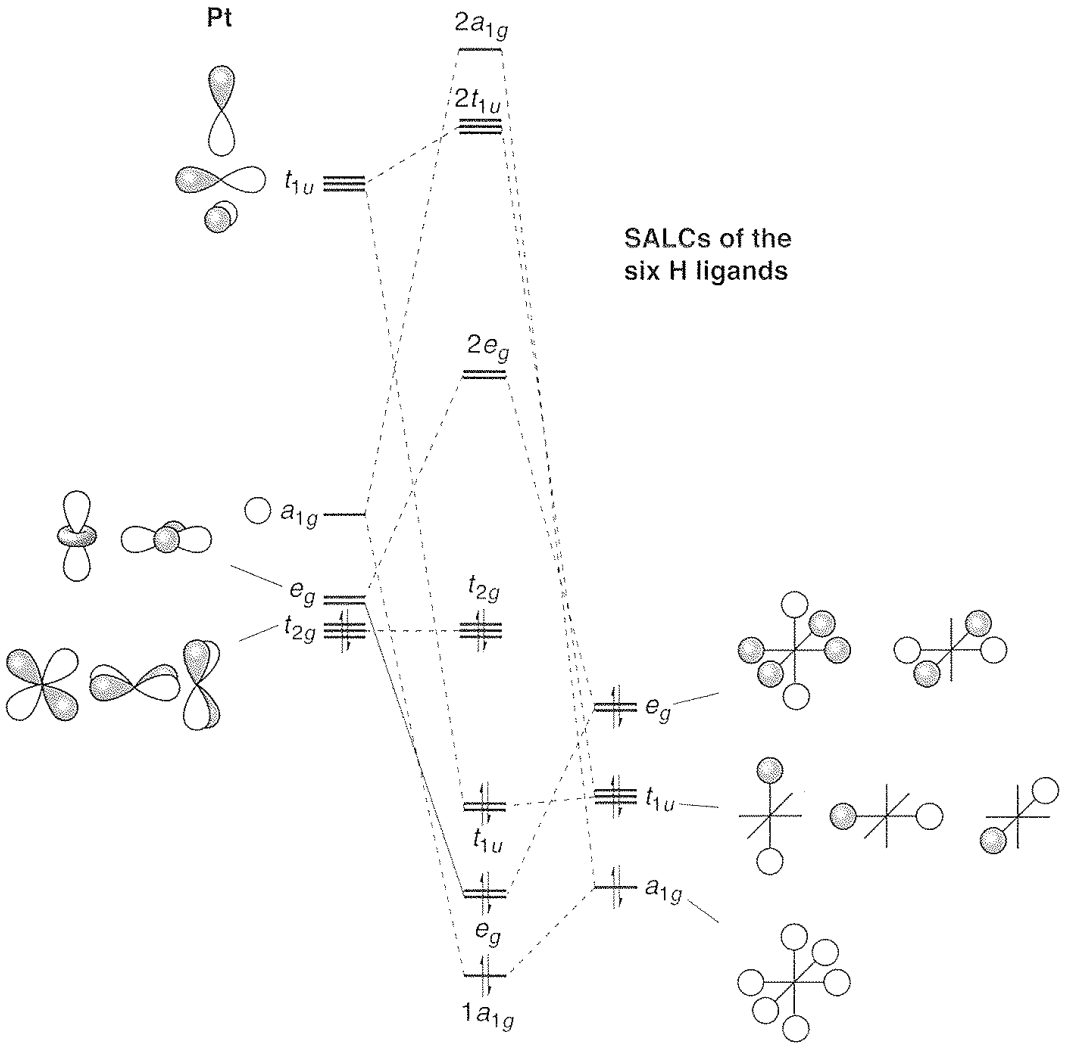
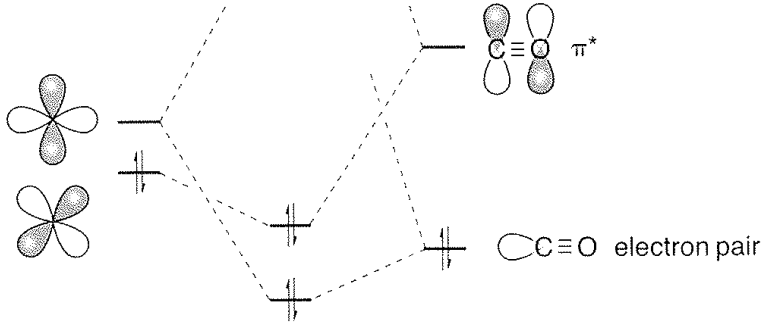
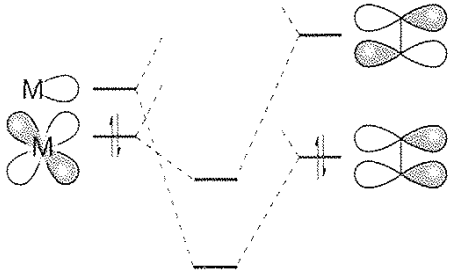
MO Beschreibung von Komplexen



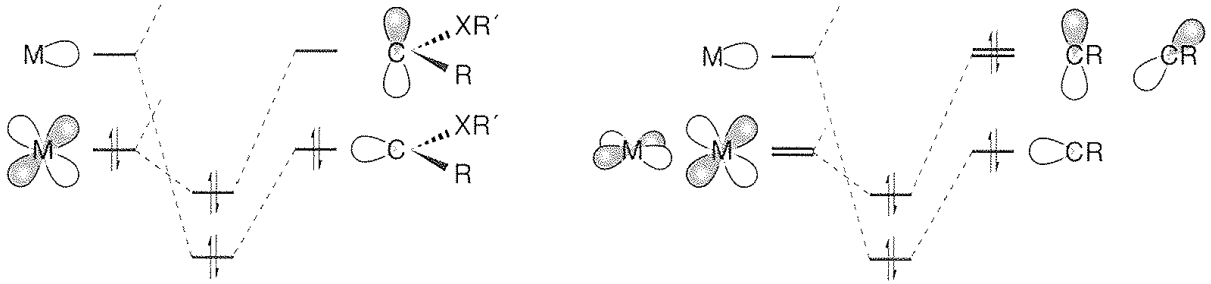
π-Bindung



The orbitals involved in the π-bonding of a carbonyl ligand.

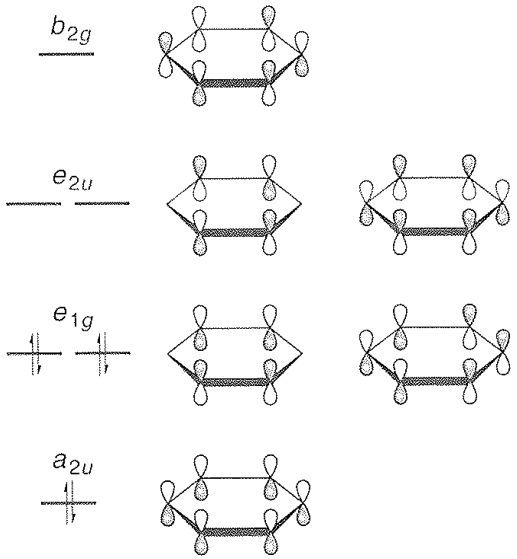


Orbital interactions in the Chatt–Dewar–Duncanson bonding model of olefin binding.

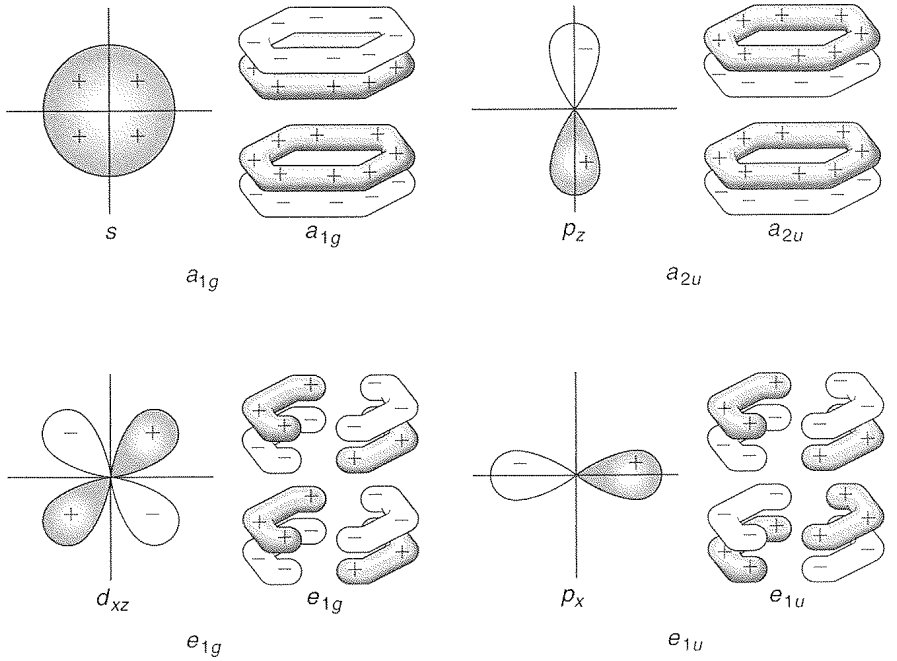


π-Bonding in Fischer carbene (left) and carbyne (right) complexes.

π-Donor Liganden

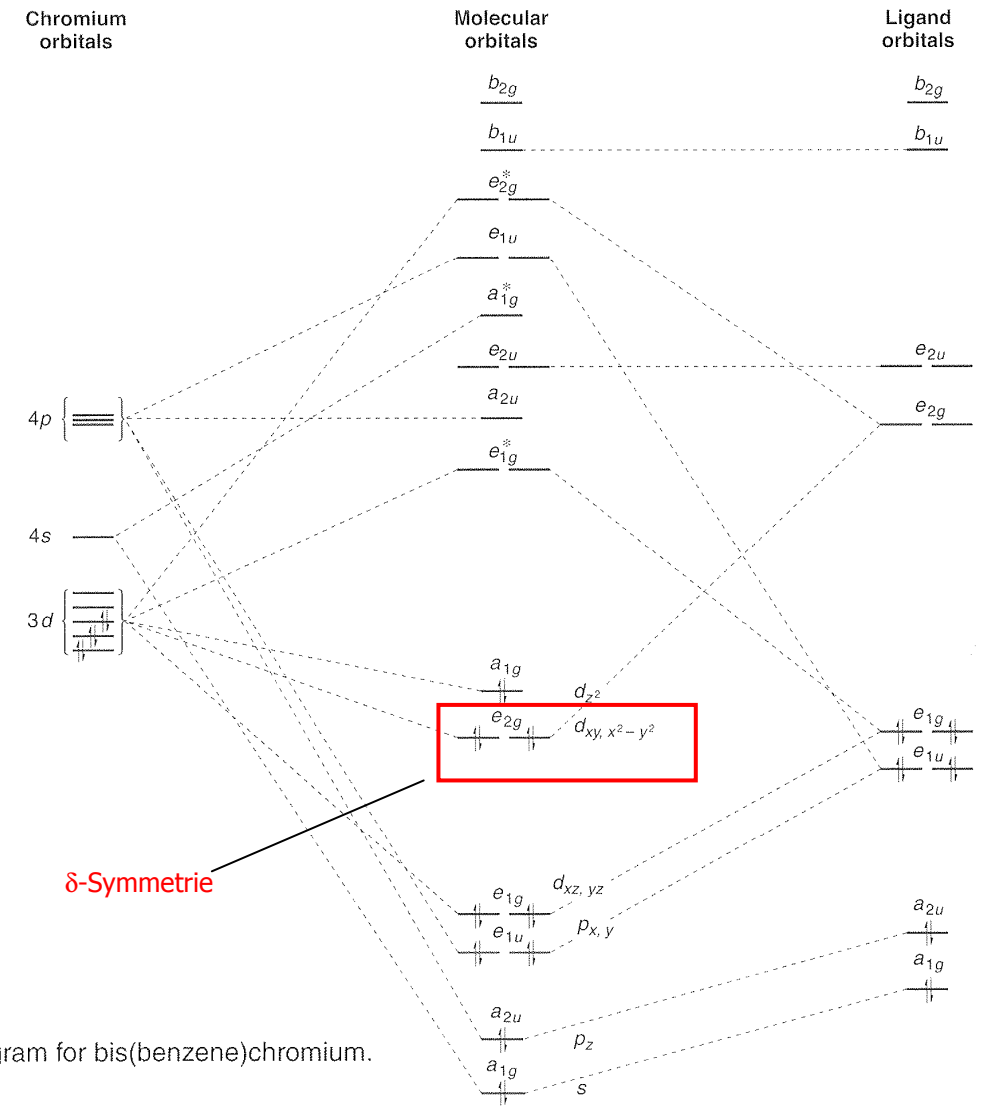


Molecular orbitals for the π-system of benzene.



The combinations of metal and ligand orbitals that form the molecular orbitals of bis(benzene)chromium.

π-Donor Liganden



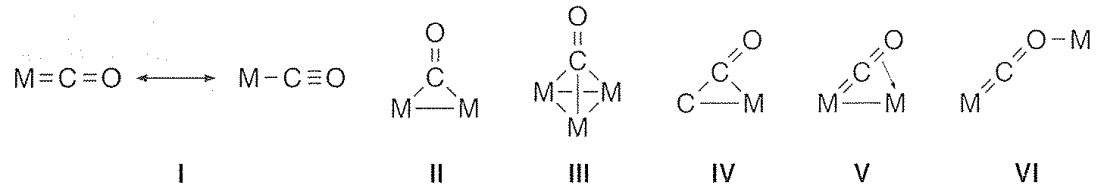
Molecular orbital diagram for bis(benzene)chromium.

Carbonyl Liganden

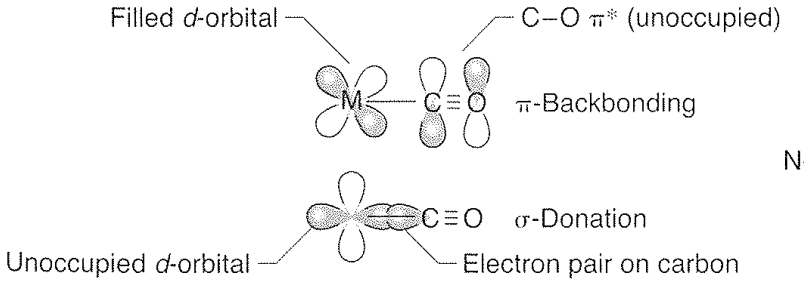
Stable neutral binary metal carbonyls.

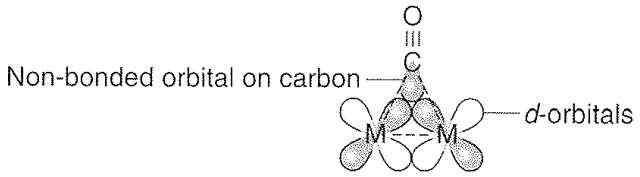
$V(CO)_6$*, $Cr(CO)_6$*, $Mn_2(CO)_{10}$*, $Fe(CO)_5$*, $Co_2(CO)_8$*, $Ni(CO)_4$*
$Fe_2(CO)_9$*, $Co_4(CO)_{12}$*
$Fe_3(CO)_{12}$*, $Co_6(CO)_{16}$
$Mo(CO)_{16}$*, $Tc_2(CO)_{10}$, $Ru(CO)_5$
$Ru_3(CO)_{12}$*, $Rh_4(CO)_{12}$*
$Rh_6(CO)_{16}$*
$W(CO)_6$*, $Re_2(CO)_{10}$*, $Os(CO)_5$
$Os_3(CO)_{12}$*, $Ir_4(CO)_{12}$*
$Ir_6(CO)_{16}$

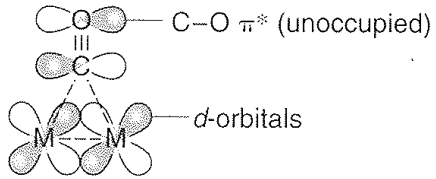
*Commercially available.



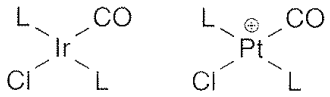
Classification of metal carbonyl complexes.







Carbonyl Liganden



1860

A

2100

B

$Ni(CO)_4$

2057

C

$Co(CO)_4^-$

1886

D

$Fe(CO)_4^{2-}$

1785

E

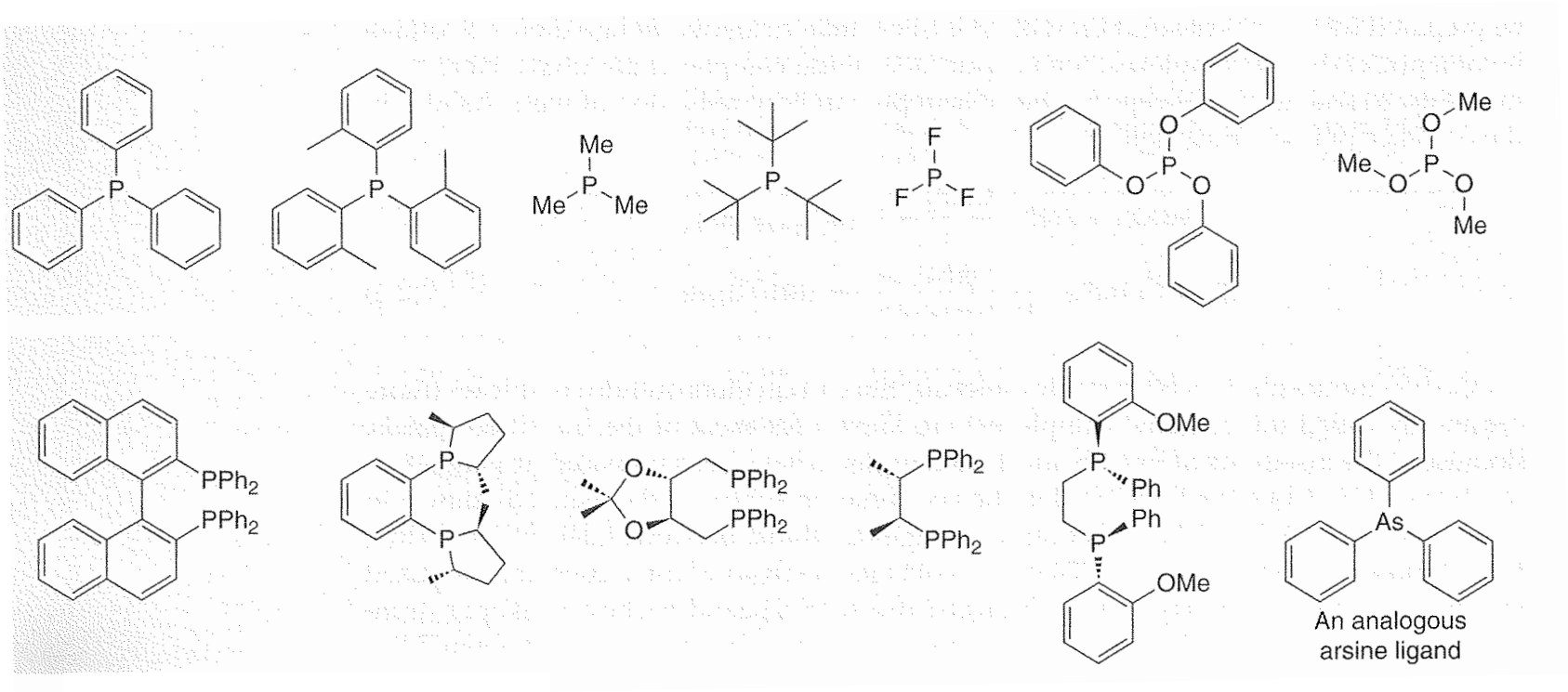
L = PPh_3

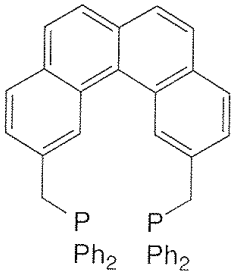
CO stretching frequencies of five different metal carbonyl compounds.

Selected M–CO bond dissociation energies (BDE) from theory and experiment.

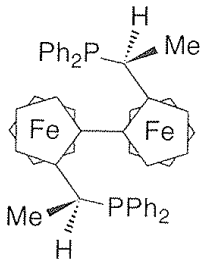
M–CO	Calculated first BDE (kJ/mol)	Experimental first BDE (kJ/mol)	Calculated mean BDE (kJ/mol)[48]	Experimental mean BDE (kJ/mol)
$V(CO)_6^-$	171[48]			
$Cr(CO)_6$	147[48]	162,[53] 155[54]	107	110[55]
$Mo(CO)_6$	119[48]	126,[53] 142[54]	126	151[55]
$W(CO)_6$	142[48]	166,[53] 159[54]	156	179[55]
$Mn(CO)_6^+$	92[48]			
$Rh(PPr^i_3)_2Cl(CO)$	35[56]	36		
$Ir(PPr^i_3)_2Cl(CO)$	84[56]	> 72		
$Ni(CO)_4$	106[48]	104[53]	179	191[55]
$Pd(CO)_4$	27[48]		44	
$Pt(CO)_4$	38[48]		59	

Phosphan Liganden

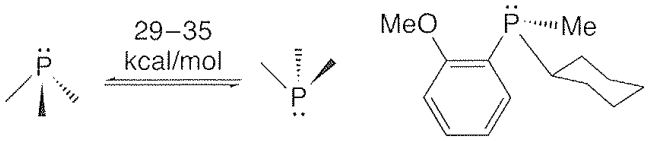




Transphos



Ph-Trap



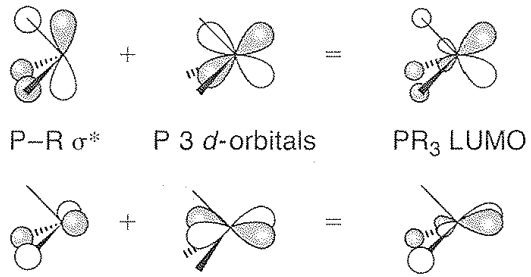
Barrier to interconversion and one of the first ligands for asymmetric hydrogenation.

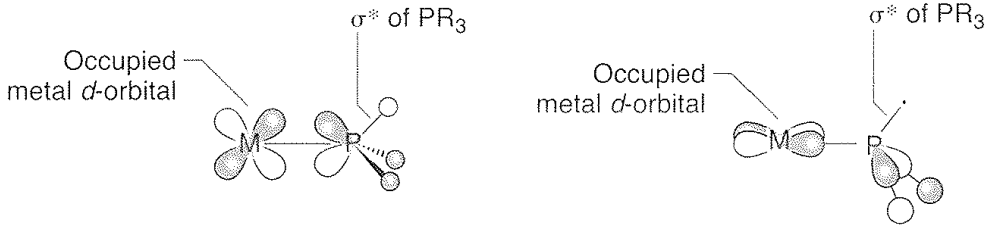
Phosphan Liganden

PR_3	ΔH_{HP} (kcal/mol)[a]	pK_a
$(p\text{-}ClC_6H_4)_3P$	17.9 (0.2)[b]	1.03[c]
$(p\text{-}FC_6H_4)_3P$	19.6 (0.2)	1.97[c]
Ph_3P	21.2 (0.1)	2.73[d]
$(o\text{-}MeC_6H_4)_3P$	22.6 (0.2)	3.08[c]
$(p\text{-}MeC_6H_4)_3P$	23.2 (0.3)	3.84[c]
$(p\text{-}MeOC_6H_4)_3P$	24.1 (0.2)	4.57[c]
$MePh_2P$	24.7 (0.0)	4.59[e]
Me_2PhP	28.4 (0.2)	6.50[d]
Me_3P	31.6 (0.2)	8.65[d]
$(c\text{-}C_6H_{11})P$	33.2 (0.4)	9.70[d]
Et_3P	33.7 (0.3)	8.69[d]
$Bu^t{}_3P$	36.6 (0.3)	11.4[c]

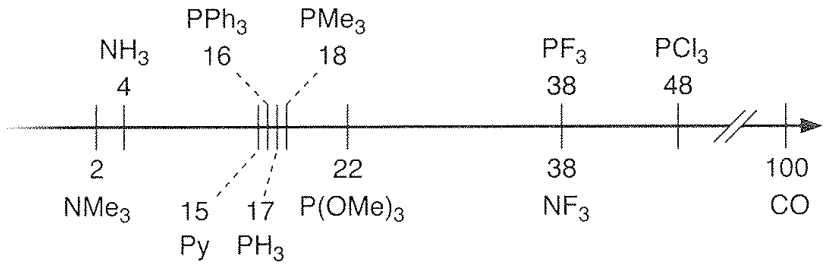
[a] For protonation with CF_3SO_3H in dichloroethane solvent at 25.0 °C.
[b] Numbers in parentheses are average deviations.
[c] Source: Allman, T.; Goel, R. G. *Can. J. Chem.* **1982**, *60*, 716.
[d] Source: Streuli, C. A. *Anal. Chem.* **1960**, *32*, 985.
[e] Source: Golovin, M. N.; Rahman, M. M.; Belmonte, J. E.; Giering, W. P. *Organometallics* **1985**, *4*, 1981.

Phosphan Liganden: Bindung





Mixing of σ*-orbitals in P(III) ligands with the phosphorus *d*-orbital and the symmetry of orbital interactions in metal–phosphine backbonding.



Calculated π-acceptor index for P- and N-based ligands, relative to CO, determined by a natural bond orbital (NBO) analysis. (Taken from Figure 3 of *Organometallics* **2007,** *26,* 2637.)

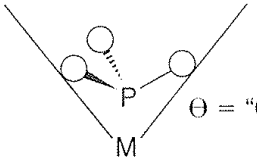
Table 2.5. Representative ν_{CO} values for $[Ni(CO)_3L]$.[a]

L	ν_{CO} (cm^{-1})
PBu^t_3	2056
PCy_3	2056
PMe_3	2064
$P(C_6H_4\text{-}4\text{-}OMe)_3$	2066
PPh_3	2069
$P(OMe)_3$	2079
$P(OPh)_3$	2085
PF_3	2110

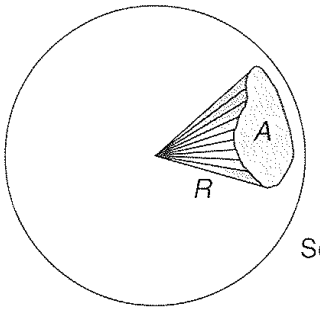
[a] Source: Tolman, C. A. *Chem. Rev.* **1977**, 77, 313.

Phosphan Liganden: Sterische Eigenschaften

Phosphorus ligand	Cone angle (°)	Solid angle (°)[c]
PH_3	87	
$P(OCH_2)_3CR$	101	82
PF_3	104	
$P(OMe)_3$	107	113
PMe_3	118	124
PMe_2Ph	122	126
$Ph_2PCH_2CH_2PPh_2$	123	
$PHPh_2$	128	112
$P(OPh)_3$	128	135
PEt_3	132	143
PPh_3	145	129
$PPh_2(Bu^t)$	157	149
$PPh(Bu^t)_2$	170	168
PCy_3	170 (163–181)[b]	181
$P(Bu^t)_3$	182	
$P(o\text{-tol})_3$	194 (183–198)[b]	142
$P(mesityl)_3$	212	



Θ = "Cone angle"

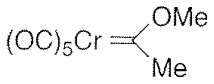


Solid angle = $\frac{A}{R^2}$

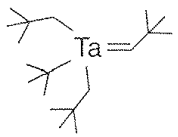
A = Area of shadow

R = Distance from light source to sphere

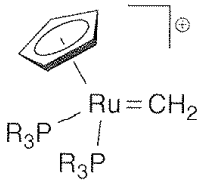
Carben Liganden



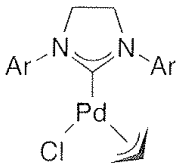
A The first "Fischer carbene complex"



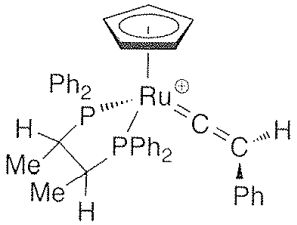
B The first "Schrock carbene complex"



C Hybrid of a Fischer and Schrock carbene complex

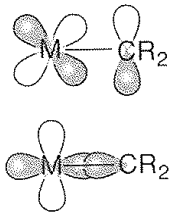


D *N*-Heterocyclic carbene compex

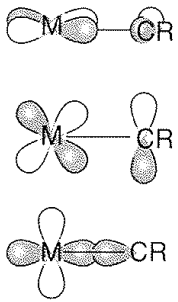


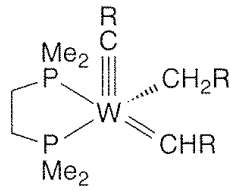
E Vinylidene complex

The carbon of N-heterocyclic carbenes is very soft and less electronegative than most heteroatom Lewis bases. Relative to phosphanes carbene are stronger σ-donors, have stronger M-L bond strength and have two-fold symmetry.

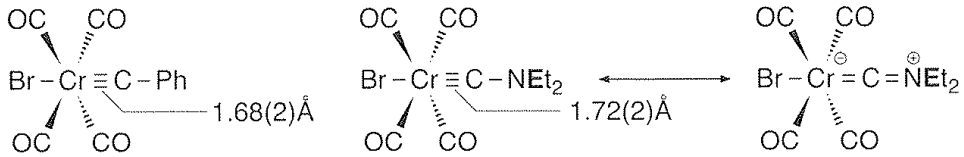


Carbin Liganden

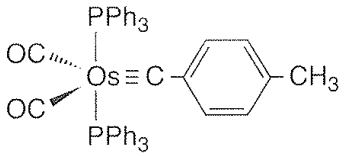




	Bond length (Å)	W–C–C
W ≡ C	1.785(8)Å	175°
W = C	1.942(9)Å	150°
W – C	2.258(9)Å	124°



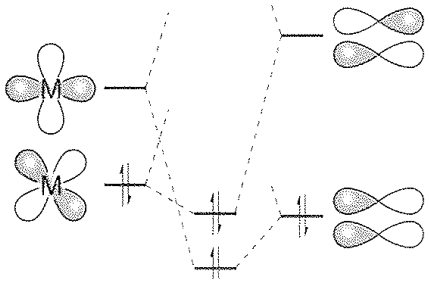
X-ray diffraction data of a complex with a carbyne, carbene, and alkyl group and two carbyne complexes with different substituents.

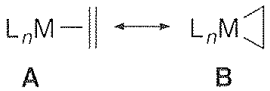


$\nu_{Os \equiv C}$	: 1375 cm^{-1}
ν_{CO}	: 2010 and 1944 cm^{-1}
^{13}C NMR CO	: δ 183 (t, $^{2}J_{CP}$ = 9.5 Hz)
Os ≡ C	: δ 331 (t, $^{2}J_{CP}$ = 11 Hz)

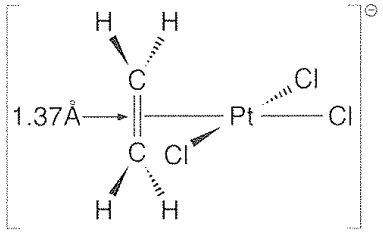
Spectroscopic data of a carbyne complex.

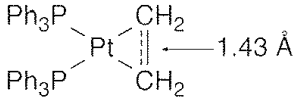
Olefin Komplexe



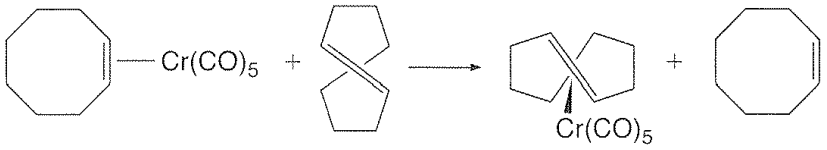


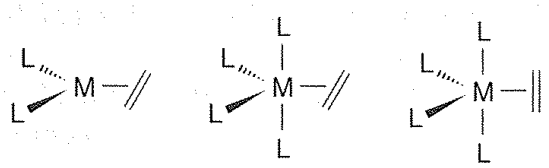
Orbital symmetries and the valence bond description of transition metal olefin complexes.





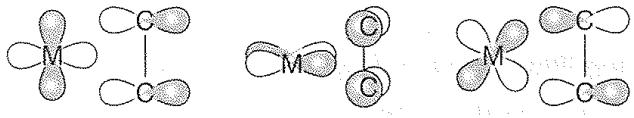
Changes in C–C distances upon binding of ethylene to an electron-poor Pt(II) and electron-rich Pt(0) center.



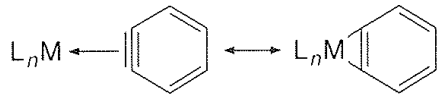


Orientation of olefins in d^{10} trigonal planar, d^{8} trigonal bipyramidal, and d^{6} trigonal bipyramidal complexes.

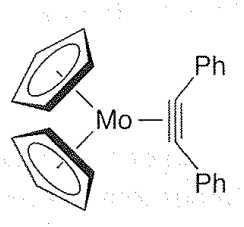
Alkin Komplexe

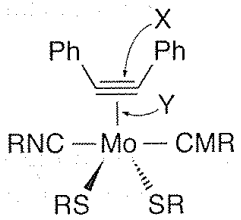


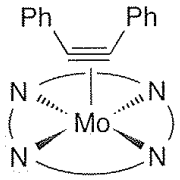
The three bonding interactions of metal–alkyne complexes.



Resonance structures of benzyne complexes.





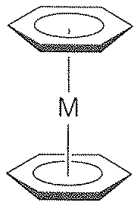


		R = *t* Bu	Mo (TPP)(PNC≡CPh)
X (Å)	1.27	1.28	1.32
Y (Å)	2.05	1.90	1.85

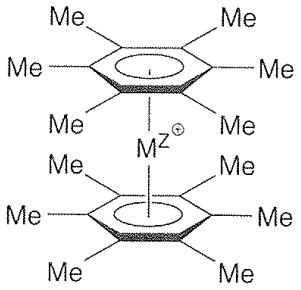
TPP = tetraphenylphorphyrin

Effect of acetylene π-donation on the structures of metal–alkyne complexes.

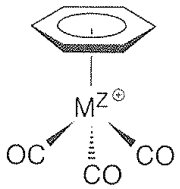
Aren Komplexe



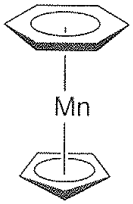
M = Cr, Mo, or W

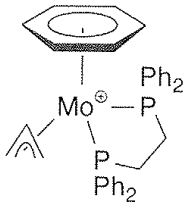


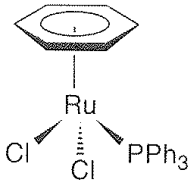
Z = 1; M = Tc or Re
Z = 2; M = Fe, Ru, or Os



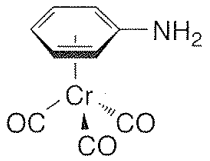
Z = 1; M = Mn
Z = 0; M = Cr, Mo, or W



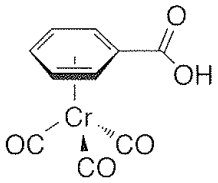




Representative η^6-arene complexes.



Less basic than aniline



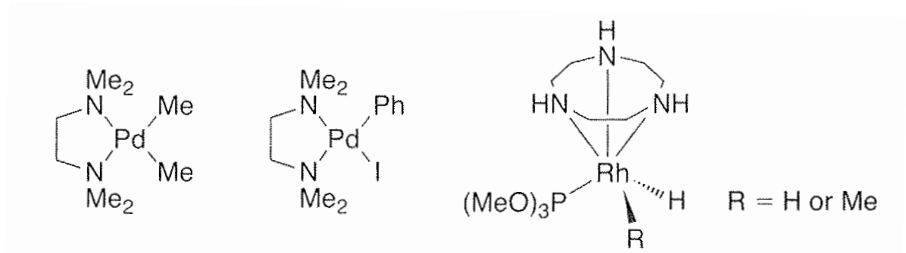
More acidic than benzoic acid

Effect of acid-base properties from arene binding.

Franz Hein, University of Leipzig, 1935

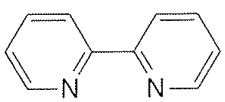
Vgl D. Seyferth: *Organometallics* **2002,** *21,* 1520 und *Organometallics* **2002,** *21,* 2800

Amin Komplexe

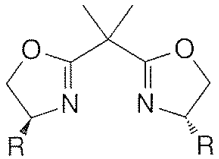


Amine	Cone angle (°)[a]
NH_3	94
NH_2Et	106
$NHEt_2$	125
NEt_3	150
NPr^i_3	160
NPh_3	166
NPr^i_3	220

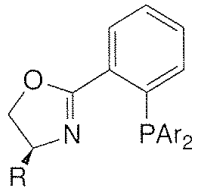
[a]For comparison, the cone angle of PEt_3 is 132° (see Table 2.6).



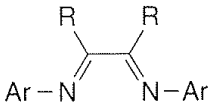
Bipyridine



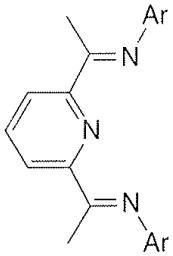
Bisoxazoline



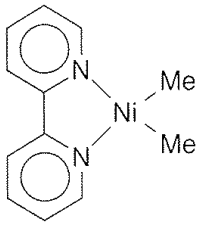
Phosphinooxazoline

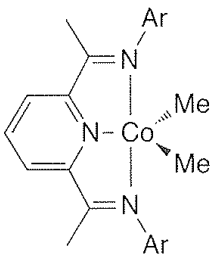


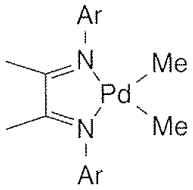
Bis-imine or
α-diimine

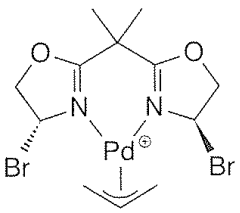


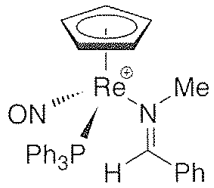
Pyridyl
bis(imine)



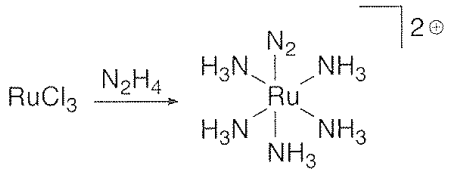


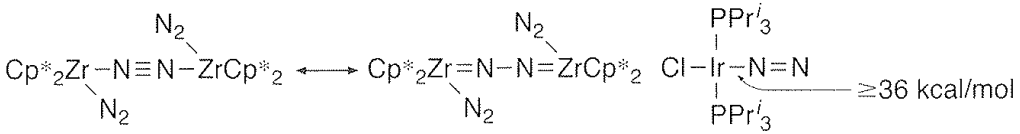




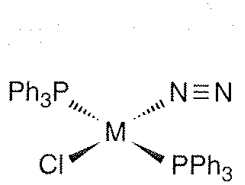


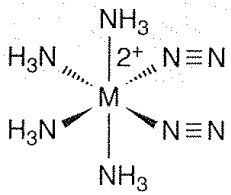
Distickstoff Komplexe

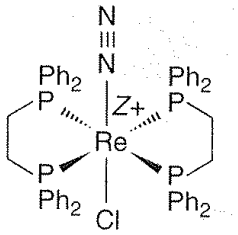




Two of the most stable N_2 complexes.





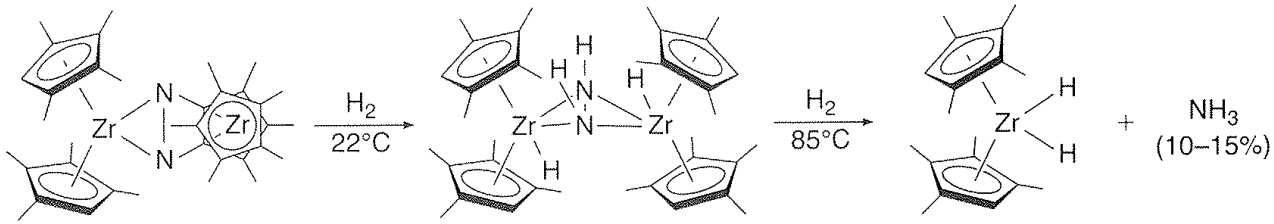


M = Rh ν_{N_2} = 2152 cm^{-1}
M = Ir ν_{N_2} = 2105 cm^{-1}

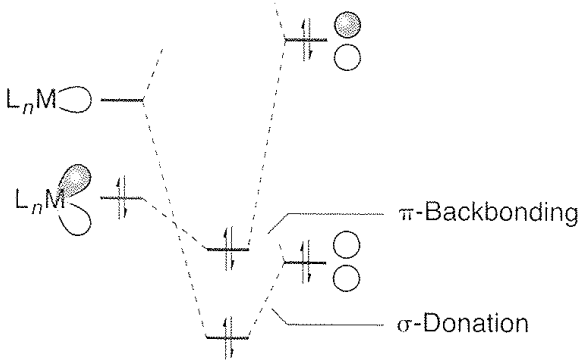
M = Ru ν_{N_2} = 2220 and 2185 cm^{-1}
M = Os ν_{N_2} = 2175 and 2120 cm^{-1}

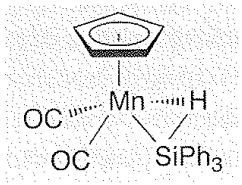
Z = O ν_{N_2} = 1980 cm^{-1}
Z = + 1 ν_{N_2} = 2060 cm^{-1}

N_2 stretching frequencies for several N_2 complexes.

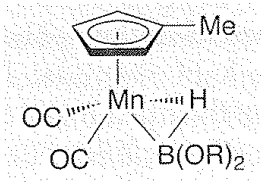


Sigma Komplexe

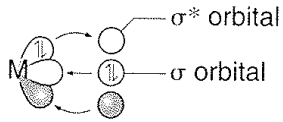




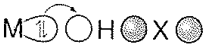
First silane σ-complex



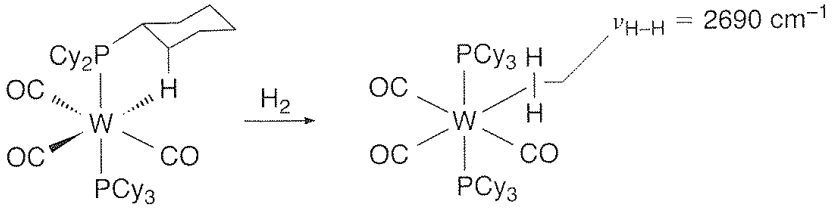
A borane σ-complex



versus



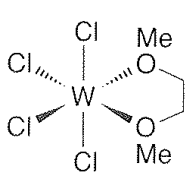
Hydrogen bonding

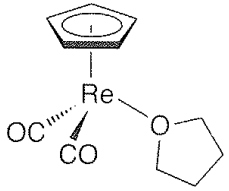


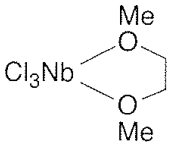
For product of addition of H–D J_{H-D} = 33.5 Hz
(versus 43.2 Hz for free H–D)

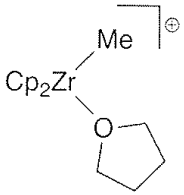
The bonding between a metal and an X-H σ-bond is weaker than the bonding between a metal and a π-bond, because the σ-bond is lower in energy and thus less basic while the σ*orbital is higher in energy and therefore less π-acidic.

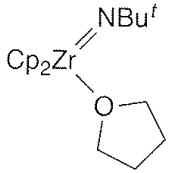
Ether und Schwefel Komplexe

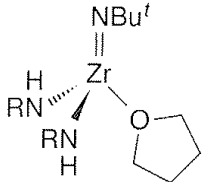


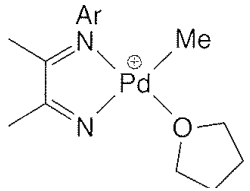


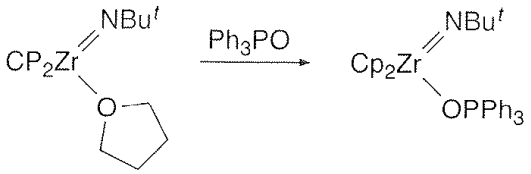


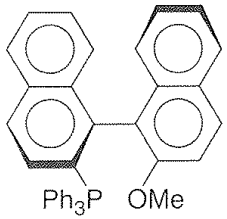




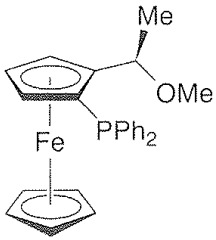


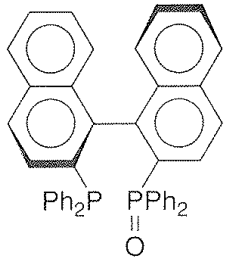




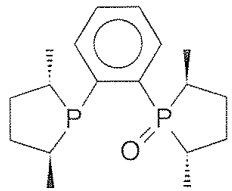


MOP

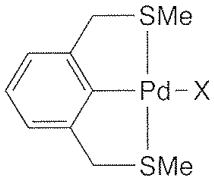


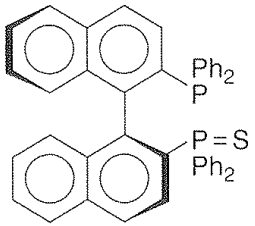


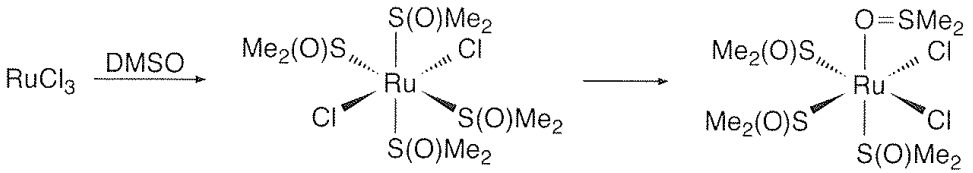
BINAP monoxide



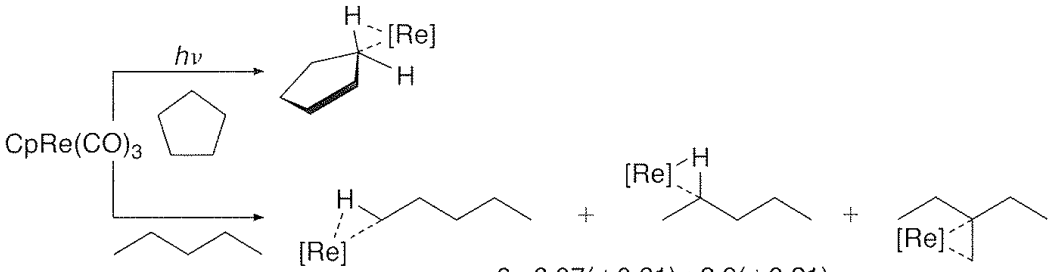
DuPhos monoxide



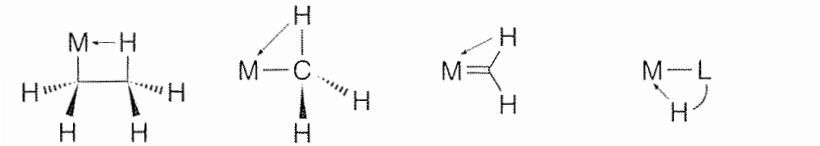




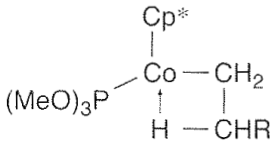
Alkane Komplexe und Agostische Wechselwirkung



6 : 6.07(±0.21) : 2.9(±0.21)
vs. 6 : 4 : 2 ratio of hydrogens



β-Agostic | α-Agostic | α-Agostic | Agostic interaction with a dative ligand



R = Me: J_{CH} = 38 Hz, δH = –13.2 ppm

R = H: J_{CH} = 61 Hz, $\delta^{1}H$ = –12.1 ppm, $\delta^{13}C$ = –5.8 ppm