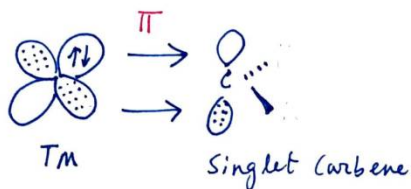
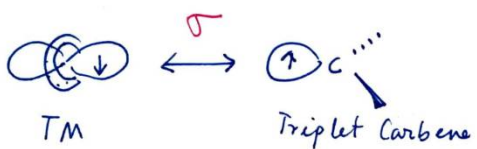


Fischer - type
Carbene Complex

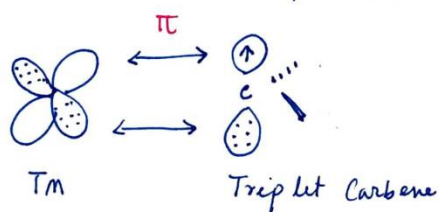


e.g. $(CO)_5Cr C(=O)NMe_2$

TM: Transition Metal



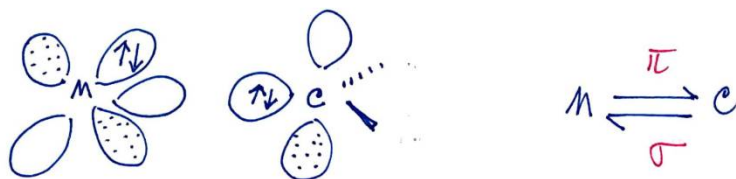
Schrock - type
Carbene Complex



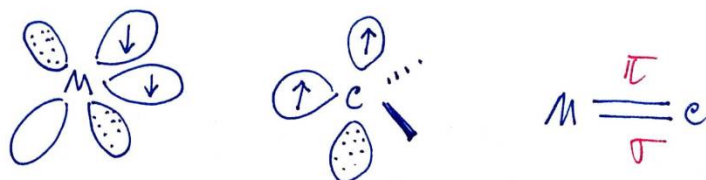
e.g. $(\eta^5-C_5H_5)_2Ta(CH_2)CH_3$

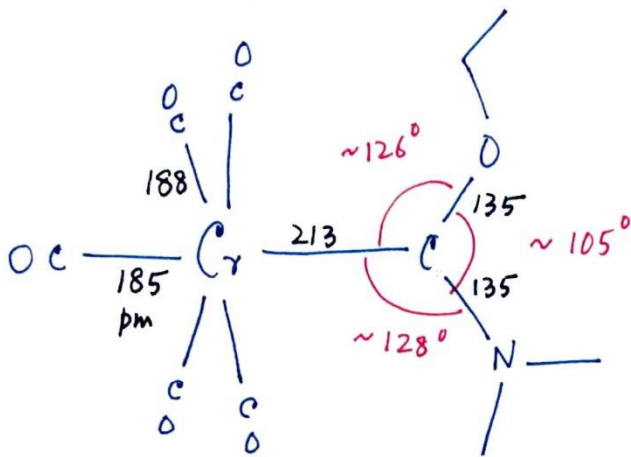
Finally ,

Fischer type :



Schrock type :





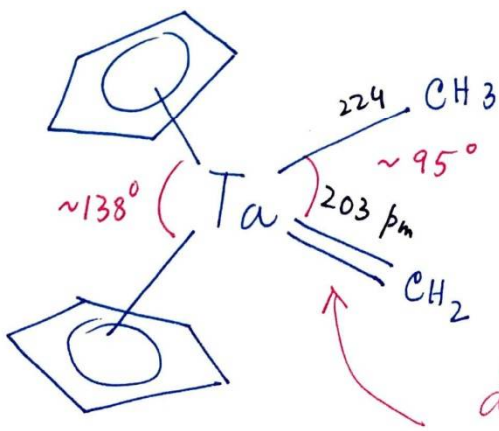
Features →

Str. of $(CO)_5CrC(OEt)NMe_2$

- #1. The Cr, C, O and N atoms are coplanar
- #2. Geometry of the carbene C is trigonal planar, hybridization is approximately sp^2
- #3. M-C (Carbene): bond is shorter than M-C single bond, but longer than M-C(CO) bond in metal carbonyls

↓
indicates $M(d\pi) \rightarrow C(p\pi)$ Bonding.

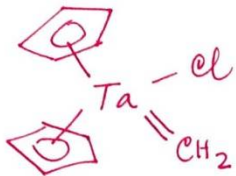
- #4. C-X bond (X = hetero atom) is shorter than $\overset{\delta-}{C}-\overset{\delta+}{X}$ single bond → $C(p\pi) \leftarrow X(p\pi)$ interaction



Str. of $(\eta^5-C_5H_5)_2Ta(CH_2)CH_3$

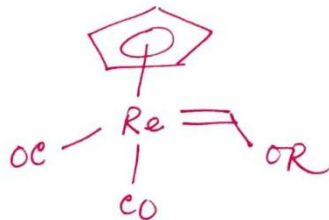
distinctly shorter bond than Ta-CH₃ single bond

- Identify the following complexes as Fischer's Carbene or Schrock - alkylidene?



- d^2 System,
- early transition metal
- neutral carbene

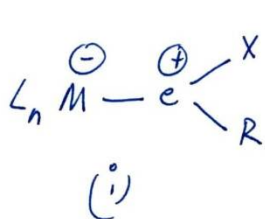
indicates Schrock's Carbene complex



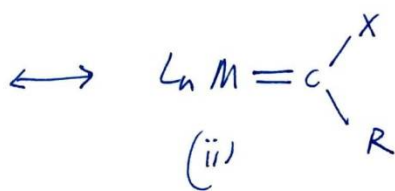
- d^6 System
- mid-transition metal
- neutral carbene

indicates a Fischer's Carbene complex

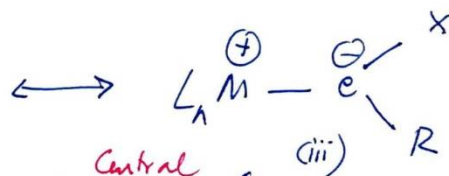
- The metal carbene bond can be described by several resonance forms



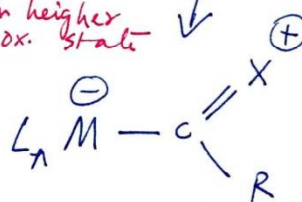
σ -bond



π -back bond



Central M-atom is in higher ox. state



(iv)

Further π -Contribution considered from the hetero atoms (X)

The σ -bond character of Fischer type carbene complexes is best represented by a M-C-X three-centred four-electron bond with the σ -electron density mainly located at either the $M(dxz)$ orbital of M or the σ orbital of the heteroatom 'X' in the carbene ligand.

However, in reality the true M=C bond order is much less than 2, as observed by x-ray crystallography, favouring the acyl form.

Organometallics 2004, 23, 2541–2551

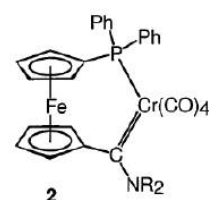
Synthesis, Structures, and Electrochemistry of Group 6 Aminocarbene with a P-Chelating 1'-(Diphenylphosphino)ferrocenyl Substituent

Luděk Meca,[†] Dalimil Dvořák,[†] Jiří Ludvík,[†] Ivana Císařová,[§] and
Petr Štěpnička^{*§}

Table 2. Selected Bond Distances (Å) and Angles (deg) for 2b^a

Fe–Cg(1)	1.6448(8)	Fe–Cg(2)	1.6391(8)
Cr–P	2.4092(6)	Cr–C(28)	1.848(2)
P–C(6)	1.809(2)	C(28)–O(2)	1.157(2)
P–C(16)	1.833(2)	Cr–C(29)	1.890(2)
P–C(22)	1.842(2)	C(29)–O(3)	1.155(2)
Cr–C(11)	2.139(2)	Cr–C(30)	1.888(2)
C(1)–C(11)	1.500(2)	C(30)–O(4)	1.151(2)
C(11)–N	1.325(2)	Cr–C(31)	1.854(2)
N–C(12)	1.475(2)	C(31)–O(5)	1.155(2)
N–C(15)	1.491(2)	C(12)–C(13)	1.515(3)
O(1)–C(13)	1.428(2)	C(14)–C(15)	1.515(3)
O(1)–C(14)	1.424(2)		
Cp(1)–Cp(2)	2.1(1)	C(11)–N–C(12)	124.6(2)
P–Cr–C(11)	90.15(5)	C(11)–N–C(15)	127.4(2)
C(6)–P–C(16)	103.97(8)	C(12)–N–C(15)	109.0(1)
C(6)–P–C(22)	100.75(8)	N–C(12)–C(13)	109.5(2)
C(16)–P–C(22)	99.50(8)	N–C(15)–C(14)	108.8(2)
C(1)–C(11)–N	111.0(1)	C(13)–O(1)–C(14)	110.1(1)

^a Definitions of the ring planes: Cp(1), C(1)–5; Cp(2), C(6)–10). Cg(1) and Cg(2) are the respective ring centroids.



R = morpholin-4-yl

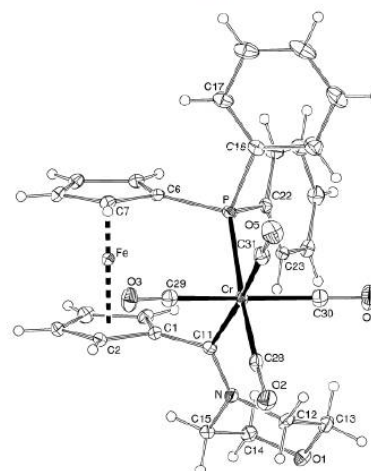
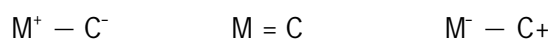


Figure 3. View of the molecular structure of 2b. Thermal motion ellipsoids are drawn at the 30% probability level.

	Fisher carbene	Schrock carbene
(1)Shape	Bent and Singlet	Linear and Triplet
(2)Carbene	Electron deficient. Stabilized by heteroatom groups. Attacked by nucleophiles.	Electron rich. Destabilized by heteroatom groups. Attacked by electrophile.
(3)Metal	In low oxidation state. Electron rich. Attacked by electrophile. Stabilize by electron accepting ligand.	In high oxidation state. Electron poor. Attacked by nucleophile. Stabilize by electron donating ligand.
(4)M=C	Relative weak. Low rotational barrier.	Relative strong. Large rotational barrier.

The M=C bond can be polarized in one way or the other given the large flexibility of electronic properties of transition-metal fragments.



One can distinguish the cationic or neutral complexes of electrophilic carbene of Pettit type, that tend to behave somewhat as carbocations coordinated to transition metals, and the neutral metal complexes of nucleophilic carbene complexes of Schrock type that tend to react as ylids.

It has been suggested that complexes of electrophilic carbenes be considered as the combination of a metal fragment with a singlet carbene, a ligand, whereas the complexes of nucleophilic carbenes are the combination of a metal fragment with a triplet carbene, an X_2 ligand (as shown in scheme below). Free methylene is a triplet in the ground state and has a low-energy singlet excited state. Carbene-bearing electron withdrawing substituents such as Fischer's carbenes are singlets. However, Pettit's iron-methylene species has a strongly electrophilic methylene, which is explained by the positive charge and electron-withdrawing carbonyl ligands.

