

2.3: Electron Counting in Transition Metal Complexes

Electron counting is always important in chemistry, especially when reactions are occurring. Because reactions involve the transfer of electrons from one atom to another during the making and breaking of chemical bonds, we need to keep track of where the electrons are going.

Counting electrons on a transition metal in a coordination compound can be a little tricky. Instead of an eight-electron rule or octet, transition metals obey an eighteen electron rule. The easiest way to count electrons is to take the complex apart and count the electrons in pieces. First, we give the donated electrons back to the individual ligands.

- Deconstruct the complex: give lone pairs back to ligands

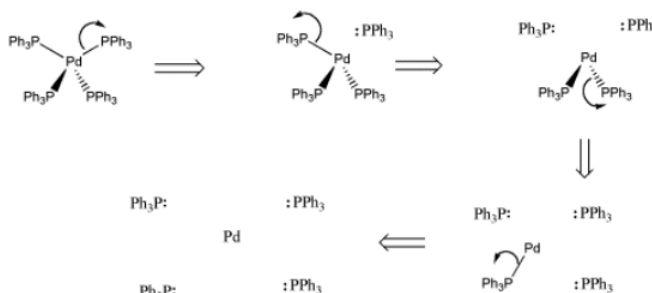


Figure 2.3.1: Giving each pair of donor electrons back to the ligands in a coordination complex.

Once the complex has been deconstructed, we count a pair of electrons for each ligand, since they are each donating a pair to the metal in the complex. Also, we must count the valence electrons that the metal brings itself. The total is the electron count in the metal in the complex. It often equals eighteen.

- Count one pair of electrons per ligand
- Count the valence electrons on the metal

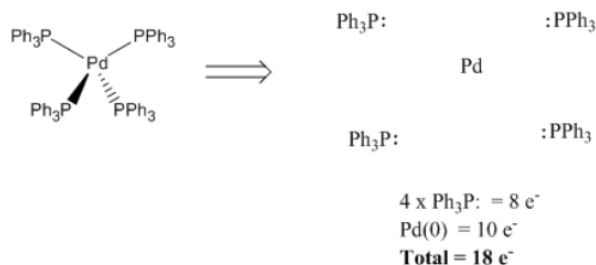


Figure 2.3.2: Counting electrons on the ligands and the metal.

There is a wrinkle in this process if charges are involved. For example, if the free ligands are not neutral, but charged, you need to adjust the electron count on the metal. The metal may be an ion, not an atom, so the electron count will be lower. If donor atoms have formal charges, adjust the charge on the metal atom or ion to balance the overall charge on the complex. In many cases, the overall charge is zero, so the metal charge is just the sum of charges on ligands.

If you don't remember anything about formal charges, [review here](#).

- Check for formal charges on free ligand donor atoms
- Adjust charge on metal so that the overall charge of (ligands + metal) equals the charge on the complex

For example, in *cis*-platin, two of the ligands are chlorides, which have negative charges. Since *cis*-platin is neutral overall, the platinum must have a two plus charge. As a result, it does not have ten electrons. It only has eight. The total electron count on the metal in the complex is sixteen.

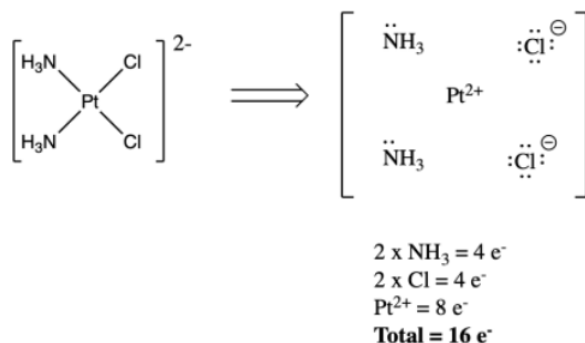


Figure 2.3.3: Counting electrons on the anionic ligands and the metal ion.

A further wrinkle occurs if there is an overall charge on the complex. In main group, covalent compounds, we always adjust the electron count to reflect an overall charge on the structure. We don't have to do that here, because we already make the adjustment when we decide the "oxidation state" or charge on the metal.

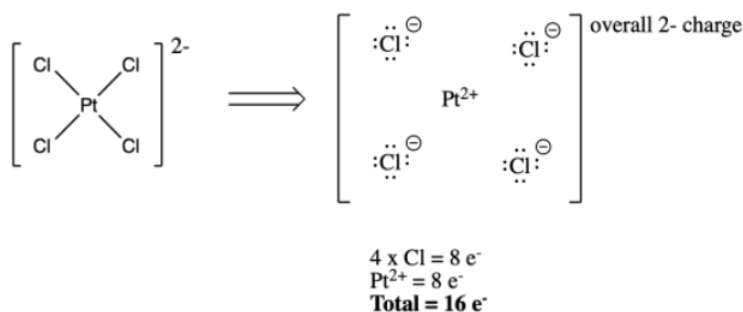

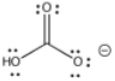
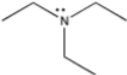

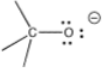
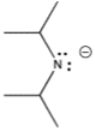


Figure 2.3.4: Counting electrons on the ligands and the metal ion in an overall anionic complex.

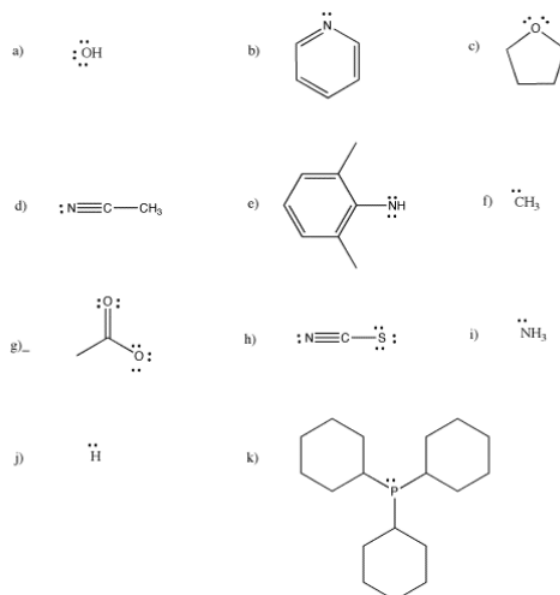
Anionic ligands are often prepared by deprotonating a neutral molecule. Some common bases used in synthetic chemistry are shown below. A range of base strengths are needed to ensure complete removal of proton from a variety of reactants. On the other hand, very large pKa differences between the acid reactant and the conjugate acid produced in the reaction, can cause highly exothermic reactions and lead to fires.

Table CC 2.3.1: Some bases commonly used in synthetic chemistry.

Base (counterions omitted)	Approximate pK _a of conjugate acid
	5
	7
NH_3	9
	11
	15
	17
	35
H^-	36
$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3^-$	45

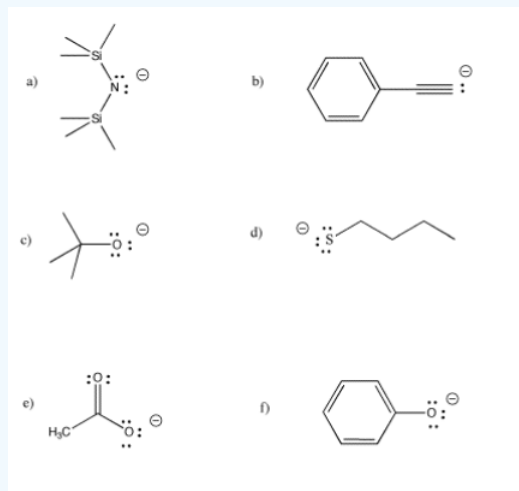
? Exercise 2.3.1

Which of the following ligands are anionic, and which ones are neutral?



? Exercise 2.3.2

For the following ligands, show the corresponding neutral (the conjugate acid). Select an appropriate base to deprotonate it, and justify your choice.



? Exercise 2.3.3

Draw structures for the following complexes (or complex ions), then deconstruct them into ligands and metal atoms (or ions).

- a) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ b) $[\text{Fe}(\text{CN})_6]^{3-}$ c) $[\text{Co}(\text{NH}_3)_6]^{2+}$
 d) $[\text{MnO}_4]^-$ e) $\text{Fe}(\text{CO})_5$ f) $[\text{PtCl}_6]^{2-}$
 g) $\text{Mo}(\text{CO})_6$ h) $[\text{WO}_4]^{2-}$ i) $(\text{PPh}_3)_3\text{RhCl}$
 j) $[\text{RuO}_3]^{2-}$ k) $\text{PCy}_3\text{Ir}(\text{H})(\text{CO})\text{Cl}$ (Cy = cyclohexyl)

? Exercise 2.3.4

For each complex in the previous problem, what is the valence electron count at the metal in the complex?

Answer a

Metal valence count: 9

Metal with charge: 6

Donated by ligands: $6 \times 2 = 12$

Total: 18

Answer b

Metal valence count: 8

Metal with charge: 5

Donated by ligands: $6 \times 2 = 12$

Total: 17

Answer c

Metal valence count: 9

Metal with charge: 7

Donated by ligands: $6 \times 2 = 12$

Total: 19

Answer d

Metal valence count: 7

Metal with charge: 0

Donated by ligands: $4 \times 4 = 16$

Total: 16

Answer e

Metal valence count: 8

Metal with charge: 8

Donated by ligands: $5 \times 2 = 10$

Total: 18

Answer f

Metal valence count: 10

Metal with charge: 6

Donated by ligands: $6 \times 2 = 12$

Total: 18

Answer g

Metal valence count: 6

Metal with charge: 6

Donated by ligands: $6 \times 2 = 12$

Total: 18

Answer h

Metal valence count: 6

Metal with charge: 0

Donated by ligands: $4 \times 4 = 16$

Total: 16

Answer i

Metal valence count: 9

Metal with charge: 8

Donated by ligands: $4 \times 2 = 8$

Total: 16

Answer j

Metal valence count: 8

Metal with charge: 4

Donated by ligands: $3 \times 4 = 12$

Total: 16

Answer k

Metal valence count: 9

Metal with charge: 7

Donated by ligands: $4 \times 2 = 8$

Total: 15

Charge on metal is often represented as a Roman number in parentheses. This number is formally called the oxidation state. Oxidation state refers to how many electrons an atom has lost (or gained). In cases like this one, the oxidation state is the same thing as the charge on an ion. For example, Ta(V) means a Ta^{5+} ion.

? Exercise 2.3.5

How many valence electrons are found on the following metal ions?

a) Fe(II) b) Ni(II) c) Mn(II) d) Fe(III)

e) Zn(II) f) Mn(IV) g) Cu(I) h) Au(0)

i) Cr(IV) j) Cu(II) k) Fe(IV)

Answer

Answer a

6

Answer b

8

Answer c

5

Answer d

5

Answer e

10

Answer f

1

Answer g

10

Answer h

12

Answer i

2

Answer j

9

Answer k

4

Coordination complexes most often have 18 electrons on the metal atom. That's because, for transition metals, eighteen is the number of electrons in the nearest noble gas configuration, which includes s + p + d electrons. (The second and third row of transition metals have f electrons, too, but we usually simplify and don't worry about those electrons for electron counting purposes; we treat them like core electrons, not valence electrons.) Frequent exceptions include 16 electron complexes, which are especially common in late metals such as copper, nickel and palladium. There are molecular orbital considerations that contribute to these exceptions.

Occasionally, electron counts can be as low as eight electrons. These cases often occur in early transition metals, such as titanium or tantalum. These metals have a long way to go to get to eighteen electrons, and sometimes they cannot fit that many ligands in their "coordination sphere". Hence, steric factors can prevent metals from reaching eighteen electrons.

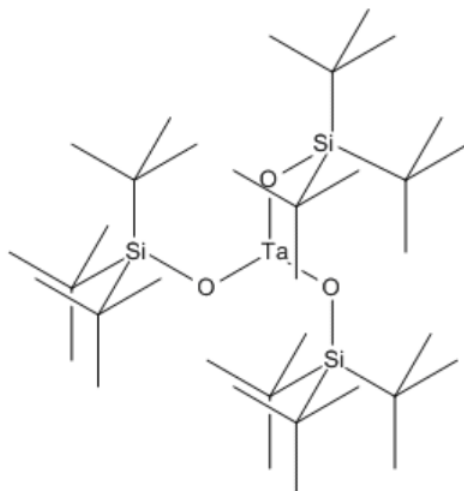


Figure 2.3.7: $(\text{SiOx})_3\text{Ta}$, or $(^t\text{Bu}_3\text{SiO})_3\text{Ta}$, an electronically unsaturated metal complex.

Complexes that do not have eighteen electrons are sometimes called "electronically unsaturated". Like six electron complexes in main group chemistry, they often react with donors in order to increase the electron count at the metal atom.

? Exercise 2.3.6

Deconstruct $(\text{silox})_3\text{Ta}$ into ligands and metal atom (or ion) and confirm the electron count on tantalum

? Exercise 2.3.7

Draw the following low-valent compounds, and determine the number of valence electrons at the metal in each one.

- a) Me_3TaCl_2 b) $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Fe}$ c) $\text{W}(\text{CH}_3)_6$

Because steric crowding is one of the reasons that metals in coordination complexes may remain "electronically unsaturated" (meaning not enough electrons) or "coordinatively unsaturated" (because there aren't enough donors), it is important to pay attention to how much space a ligand will occupy. The parameter used to describe this factor is called a "cone angle". This is just the angle at the nose of the imaginary cone where the ligand attaches to the metal. The breadth of the cone, and thus the cone angle, is determined by how large the ligand is. A large cone angle indicates a large ligand; a small cone angle is associated with a smaller ligand.

For example, trimethylphosphine, $\text{P}(\text{CH}_3)_3$, has a cone angle of 118° . Triethylphosphine, $\text{P}(\text{CH}_2\text{CH}_3)_3$, is slightly larger, with a cone angle of 132° .

? Exercise 2.3.8

Predict which of the following pairs will have the larger cone angle.

- PF_3 or PH_3
- PH_3 or $\text{P}(\text{CH}_3)_3$ (also abbreviated PMe_3)
- PMe_3 or $\text{P}(\text{C}(\text{CH}_3)_3)_3$ (also abbreviated P^tBu_3)
- P^tBu_3 or $\text{P}(\text{cyclic-C}_6\text{H}_5)_3$ (also abbreviated PPh_3)

Answer

Answer a

PF_3 (104° vs 87°)

Answer b

PMe_3 (118° vs 87°)

Answer c

P^tBu_3 (182° vs 118°)

Answer d

P^tBu_3 (182° vs 145°)

This page titled [2.3: Electron Counting in Transition Metal Complexes](#) is shared under a [CC BY-NC 3.0](#) license and was authored, remixed, and/or curated by [Chris Schaller](#) via [source content](#) that was edited to the style and standards of the LibreTexts platform.