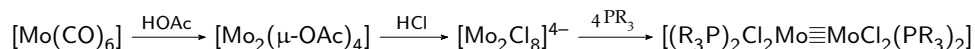


Preparation of a Quadruple Bond

Overview

From general chemistry, you are familiar with the formation of single, double and triple bonds from a σ - and up to two π -bonds. In your inorganic course, you saw that d-orbitals can overlap edge-to-edge, to also form a π -bond. What if, however, the d-orbitals overlap face-to-face? In this case, a δ -bond results. Combined with a σ - and two π -bonds, the δ -bond allows the formation of a quadruple bond between transition metals. The $[\text{Cl}_4\text{Ru}\equiv\text{RuCl}_4]^{2-}$ anion, characterized by Cotton, was the first species containing a quadruple bond identified;¹ since then, low-valence Cr, Mo, W, Tc, and Re dimers containing quadruple bonds have also been prepared. Interestingly, the chlorines of $[\text{Cl}_4\text{Ru}\equiv\text{RuCl}_4]^{2-}$ are eclipsed:^{1c} although the sterics are better in the staggered conformation, only the eclipsed allows the d-orbital overlap necessary for the δ -bond.

Quadruple bonds are generally not formed by elimination. Rather, existing quadruply-bonded systems are typically modified through ligand exchange reactions. In this project, you will prepare $[\text{Mo}_2(\mu\text{-OAc})_4]$, which contains a quadruple bond, from $[\text{Mo}(\text{CO})_6]$. Treatment of the hexacarbonyl with $\text{HCl}/\text{NH}_4\text{Cl}$ leads to a complex salt, $(\text{NH}_4)_5[\text{Mo}_2\text{Cl}_8]\text{Cl}$, in which the extra NH_4^+ and Cl^- ions are part of the crystal lattice. Although the simpler $\text{K}_4[\text{Mo}_2\text{Cl}_8]$ is known,² it is difficult to obtain pure. Treatment of these chlorides with excess trialkylphosphine leads to $[\text{Mo}_2\text{Cl}_4(\text{PR}_3)_4]$.



“ μ ” (read as “catena”) indicates that a ligand bridges two metal centers.

Notes on the Procedure

- !! Metal carbonyls are toxic and sublime easily. Work in the hood and wear gloves.
- !! Phosphines are toxic and smell wretched. Measure them by syringe in the hood. Keep the syringe in the hood until it has been rinsed with acetone, directly into the organic waste. Alkyl phosphines react with atmospheric oxygen, and therefore must be handled under N_2 . Phosphites $[\text{P}(\text{OR})_3]$ and aryl phosphines are less sensitive.
- !! Residues and washes from these reactions should be placed in the heavy-metals waste.
- Although the compounds prepared in this project are air stable as solids, their solutions are all air sensitive. See Dr. Youmans or Dr. Trujillo for advice on handling these. The library also has two excellent references, listed below.
- The gaseous HCl for the second step can be conveniently generated by slowly dripping H_2SO_4 into ~200 mL conc HCl .

References

The references on the next page may be obtained at the library or through its web-page. The 1-2 g scale on which the reactions are described is reasonable.

¹ a. Cotton, F.A.; Curits, N.F.; Johnson, B.F.G.; Robinson, W.R. *Inorg. Chem.* **1965**, *4*, 326-330. b. Cotton, F.A.; Harris, C.B. *Inorg. Chem.* **1965**, *4*, 330-333. c. Cotton, F.A. *Inorg. Chem.* **1965**, *4*, 334-336.

² Cotton, F.A.; Brencic, J.V. *Inorg. Chem.* **1970**, *9*, 351-353.

First Step:

Bignole, A.; Cotton, F.A. *Inorg. Synth.* **1972**, *13*, 81-90.

QD151 .A1 I5

Second Step:

Brencic, J.V.; Cotton, F.A. *Inorg. Chem.* **1970**, *9*, 346-351.

Third Step:

Pick your favorite phosphine (or phosphite):

Et₃P, Et₂PhP, MePh₂P:

Glicksman, H.D.; Hamer, A.D.; Smith, T.J.; Walton, R.A. *Inorg. Chem.* **1976**, *15*, 2205-2209.

Et₃P, ⁿPr₃P, ⁿBu₃P, Me₂PhP, P(OMe)₃; also ¹H and ³¹P NMR:

San Filippo, J., Jr. *Inorg. Chem.* **1972**, *11*, 3140-3143.

Airfree Techniques:

The Manipulation of Air-Sensitive Compounds, Shriver, Drezdon

QD61 .s57 1986

"Laboratory Operations with Air Sensitive Substances," Kramer, Levy, Midland

in *Organic Synthesis via Boranes*, H. C. Brown, ed.

QD412 .B1 B77

"Handling Air-Sensitive Reagents" (Aldrich Technical Bulletin AL134)

www.sigmaaldrich.com/etc/medialib/docs/Aldrich/Bulletin/al_techbull_a134.pdf