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Preparation and Characterization of a Quadruply Metal-Metal Bonded Compound

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Corresponding Author:	Tamara Powers UNITED STATES
Corresponding Author Secondary Information:	
Corresponding Author's Institution:	
Corresponding Author's Secondary Institution:	
First Author:	Tamara Powers
First Author Secondary Information:	
Order of Authors:	Tamara Powers
Order of Authors Secondary Information:	

PI Name: David C. Powers, Tamara M. Powers, Texas A&M University

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Overview:

Paddlewheel complexes are a class of compounds comprised of two metal ions (1st, 2nd, or 3rd row transition metals) held in proximity by four bridging ligands (most commonly formamidinates or carboxylates) (**Figure 1**). Varying the identity of the metal ion and the bridging ligand provides access to large families of paddlewheel complexes. The structure of paddlewheel complexes allows for metal–metal bonding, which plays a vital role in the structure and reactivity of these complexes. Due to the diversity of electronic structures that are available to paddlewheel complexes – and the corresponding differences in M–M bonding displayed by these structures – paddlewheel complexes have found application in diverse areas, such as in homogeneous catalysis and as building blocks for metal-organic frameworks (MOFs). Understanding the electronic structure of the M–M bonds in paddlewheel complexes is critical to understanding their structures and thus to application of these complexes in coordination chemistry and catalysis.

When two transition metals are held in close proximity the *d*-orbitals overlap, which can result in the formation of M–M bonds. Overlapping *d*-orbitals can form three types of bonds – σ, π, and δ – depending on the symmetry of the orbitals involved. If we assign the molecular z-axis to be coplanar with the M–M bond, a σ bond is formed by overlap of the d_{z^2} orbitals and π bonds are formed by overlap of the d_{xz} and d_{yz} orbitals. δ bonds are generated by overlap of *d*-orbitals that have two planar nodes (d_{xy} and $d_{x^2-y^2}$). As a result, all four lobes of the *d*-orbital overlap and the corresponding δ bond has two planar nodes (**Figure 2**). In theory, with the addition of δ bonds, paddlewheel complexes are capable of supporting quintuple bonds, or five bonds between metal atoms.[1] In most complexes, the $d_{x^2-y^2}$ forms strong metal–ligand bonds and does not meaningfully contribute to M–M bonding. Thus, quadruple bonds are the maximum bond order in many complexes.

In this video, we will synthesize the dimolybdenum paddlewheel complex $Mo_2(ArNC(H)NAr)_4$, where Ar = *p*-$(MeO)C_6H_4$, which features a quadruple bond. We will characterize the compound by NMR spectroscopy and use X-ray crystallography to study the M–M bond.

Principles:

We begin by constructing an MO diagram of the M–M bond within the general dimolybdenum complex $Mo_2(ArNC(H)NAr)_4$. First, we need to define our axes. Assuming the highest available symmetry, $Mo_2(ArNC(H)NAr)_4$ is in the point group D_{4h} (**Figure 3**). The z-axis is by definition assigned to the axis with highest rotational symmetry (primary axis), which in this case is a C_4 rotation axis that lies along the Mo–Mo bond. By convention, the x- and y-axis lie along the M–L bonds; in our specific case, this means that the x- and y-axes are collinear with the Mo–N vectors. According to our axis assignments, the $d_{x^2-y^2}$

orbital on each Mo atom is involved in metal–ligand bonding. That leaves us with our d_{xy}, d_{xz}, d_{yz}, and d_{z^2} orbitals for M–M bonding.

The MO diagram that describes the M–M bond in $Mo_2(ArNC(H)NAr)_4$ is shown in **Figure 4**. Linear combination of the d_{z^2} orbital on each M atom results in σ and σ* MOs. The d_{xz} and d_{yz} orbitals form π and π* MOs. Finally, linear combination of the d_{xy} atomic orbitals gives rise to the δ and δ* MOs. The δ bond exhibits the least amount of spatial overlap between the atomic orbitals and, as a result, the relative *energy* of the bonding orbitals is σ < π < δ (**Figure 2**). This corresponds to *bond strengths* where a σ bond is stronger than a π bond, which is stronger than a δ bond. We fill the corresponding MOs with the total number of *d* e^- for both Mo center, which is 8 (Mo^{2+}, d^4). This leads to a bond order of 4, which is consistent with a quadruple bond.

In this video we will use X-ray crystallography to observe the Mo–Mo bond length in the $Mo_2(ArNC(H)NAr)_4$ complex. With the Mo–Mo bond distance from solid state structure, we can find the formal shortness ratio (FSR), which is the normalized value of the M–M bond. The FSR is calculated for a bond A–B using equation 1, which is simply the ratio of the bond distance observed in the solid state ($D_{\mathrm{A-B}}$) to the sum of the atomic radii (R_1^{A} and R_1^{B}) of the individual atoms.

$$\mathrm{FSR_{AB}} = \frac{D_{\mathrm{A-B}}}{R_1^{\mathrm{A}}+R_1^{\mathrm{B}}} \qquad (1)$$

The FSR value is normalized for atomic radius and thus provides a fast and convenient way to compare M–M bond distances, not only between different metal types, but also to bond distances between non-metal atoms.

Procedure:

1. Synthesis of ligand ArN(H)C(H)NAr, where Ar = *p*-(MeO)C_6H_4 (**Figure 5**).[2]

    1.1. Combine 6.0 g (0.050 mol) of *p*-anisidine and 4.2 mL (0.025 mol) of triethylorthoformate in a 100 mL round bottom flask with a magnetic stir bar.

    1.2. Attach a distillation head to the reaction flask.

    1.3. With stirring, heat the reaction in an oil bath to reflux (120 °C). Once reflux is achieved, the byproduct ethanol should begin to distill from the reaction. Collect the ethanol in a beaker placed at the end of the distillation head.

    1.4. Heat the reaction until the distillation of ethanol ceases (at least 1.5 h).

    1.5. Remove the flask from the oil bath and allow the reaction mixture to cool to room temperature. A precipitate should form. If the product does not precipitate, place the flask in an ice bath and scratch the bottom of the flask with a spatula to encourage crystallization.

1.6. Recrystallize the product from a minimal amount of boiling toluene (for a more detailed procedure, please review the “Purifying Compounds by Recrystallization” video in the *Essentials of Organic Chemistry* series).

1.7. Collect the product by filtration through a fritted funnel and wash with 10 mL of hexanes.

1.8. Isolate the white product and allow it to dry in the air.

1.9. Collect a ^{1}H NMR of the solid using $CDCl_3$.

2. Setup of the Schlenk Line (for a more detailed procedure, please review the “Schlenk Lines Transfer of Solvent” video in the *Essentials of Organic Chemistry* series). Schlenk line safety should be reviewed prior to conducting this experiment. Glassware should be inspected for star cracks before using. Care should be taken to ensure that O_2 is not condensed in the Schlenk line trap if using liquid N_2. At liquid N_2 temperature, O_2 condenses and is explosive in the presence of organic solvents. If it is suspected that O_2 has been condensed or a blue liquid is observed in the cold trap, *leave the trap cold under dynamic vacuum*. *Do **NOT** remove the liquid N_2 trap or turn off the vacuum pump.* Over time the liquid O_2 will sublime into the pump—it is only safe to remove the liquid N_2 trap once all of the O_2 has sublimed.

2.1. Close the pressure release valve.

2.2. Turn on the N_2 gas and the vacuum pump.

2.3. As the Schlenk line vacuum reaches its minimum pressure, prepare the cold trap with either liquid N_2 or dry ice/acetone.

Commented [HK1]: Do you have a pressure gauge or how do you know when it reached the minimum pressure?

Commented [TP2]: We don’t have a vacuum gauge, we usually wait 5 minutes.

2.4. Assemble the cold trap.

3. Synthesis of $Mo_2(ArNC(H)NAr)_4$ (**Figure 6**).[1] *CAUTION: The molybdenum source used in the synthesis of $Mo_2(ArNC(H)NAr)_4$ is $Mo(CO)_6$, which is **highly toxic and may be fatal if inhaled, absorbed through the skin or swallowed**. CO is generated during the reaction. Therefore the synthesis must be conducted in a well-ventilated hood.*

3.1. Use standard Schlenk line techniques for the synthesis of $Mo_2(ArNC(H)NAr)_4$ (see the “Synthesis of a Ti(III) Metallocene Using Schlenk line Technique” video).

3.2. Add 0.34 g (1.3 mmol) $Mo(CO)_6$ and 1.0 g (3.9 mmol) of ArN(H)C(H)NAr to a 100 mL Schlenk flask and prepare the Schlenk flask for the cannula transfer of solvent.

3.3. Add 20 mL of degased *o*-dichlorobenzene to the Schlenk flask *via* cannula transfer.

Commented [HK3]: This is an interesting choice of solvent, do you use it because of the high temperature/bp?

Commented [TP4]: I actually didn’t come up with this procedure (it’s a literature reported compound). But, yes, I assume it’s the high bp.

3.4. Fit the Schlenk flask with a condenser connected to the N$_2$ gas line.

3.5. Reflux the reaction for 2 h (180 °C) in a silicone-oil bath. *NOTE: Mo(CO)$_6$ is volatile and will condense on the sides of the Schlenk flask during the reaction. To obtain higher yields, periodically re-dissolve any sublimed Mo(CO)$_6$ by pulling the flask out of the oil bath and gently swirling the solvent in the flask.*

3.6. Remove the Schlenk flask from the oil bath and allow the mixture to cool to room temperature.

Commented [HK5]: How do you know the reaction is done? Is there anyway to test it if it went to completion or is it visually obvious, such as in color change or precipitate formation?

Commented [TP6]: There isn't really a good way to determine when it's complete. The solution goes dark, but I don't think that color change indicates the reaction is done.

3.7. Filter the brown solution through a fritted funnel and wash the yellow precipitate with 10 mL of hexanes, followed by 5 mL of reagent grade acetone. The Mo$_2$(ArNC(H)NAr)$_4$ does decompose slowly in solution when O$_2$ is present. Therefore the filtration should be done promptly once the reaction is removed from N$_2$.

3.8. Collect the solid yellow Mo$_2$(ArNC(H)NAr)$_4$ and allow it to dry in air.

3.9. Using CDCl$_3$ measure the ^{1}H NMR spectrum of the product.

4. Single Crystal Growth. *Note: Mo$_2$(ArNC(H)NAr)$_4$ oxidizes slowly in solution. The crystallization solvent should be degased before use, but rigorous air-free conditions are not necessary to obtain X-ray quality crystals for single crystal X-ray diffraction.*

4.1. Degas 10 mL of dichloromethane (CH$_2$Cl$_2$) by bubbling N$_2$ gas through the solution for 10 min (see the "Synthesis of a Ti(III) Metallocene Using Schlenk line Technique" video for a more detailed procedure on purging liquids).

4.2. Make a saturated solution of Mo$_2$(ArNC(H)NAr)$_4$ by dissolving 20 mg of the solid in 2 mL of the degassed CH$_2$Cl$_2$.

4.3. Make a pipette Celite plug by inserting a small piece of Kimwipe into a pipette. Add a small amount of Celite to the pipette.

4.4. Filter the CH$_2$Cl$_2$ solution through thea pipette Celite plug into a small 5 mL vial. You can help push the solution through the Celite using a pipette bulb.

4.5. Using tweezers, insert the 5 mL vial into a 10 mL scintillation vial.

4.6. In the outer scintillation vial, add 2 mL of hexanes.

4.7. Tightly cap the scintillation vial and place it on a shelf where it will not be disturbed.

4.8. Allow at least 24 hours for single crystal growth (see the "X-ray Crystallography" video in the *Essentials of Organic Chemistry* series for a more detailed procedure on how to grow single crystals).

4.9. Collect single crystal X-ray data on the sample (see the "Single Crystal and Powder X-ray Diffraction" video for a more detailed procedure on how to collect X-ray data).

Representative Results:

Commented [HK7]: Could you provide both NMR spectra

Commented [TP8]: Yes, all results will be provided on the day of filming

Ligand ArN(H)C(H)NAr:

Yield: 3.25 g (53%). ^{1}H NMR (chloroform-*d*, 300 MHz, δ, ppm): 8.06 (s, 1H, NHC–*H*N), 6.99 (d, 4H, aromatic C–*H*, *J* = 8.7 Hz), 6.86 (d, 4H, aromatic C–*H*, *J* = 9.0 Hz) 3.80 (s, 6H, –OCH_3).

Mo complex $Mo_2(ArNC(H)NAr)_4$*:*

Yield: 450 mg (57%). ^{1}H NMR (chloroform-*d*, 300 MHz, δ, ppm): 8.38 (s, 4H, NHC–*H*N), 6.51 (d, 16H, aromatic C–*H*, *J* = 8.8 Hz), 6.16 (d, 16H, aromatic C–*H*, *J* = 8.8 Hz), 3.71 (s, 24H, –OCH_3).

Table 1. Crystal Data and Unit Cell Parameters	
Empirical formula	$C_{60}H_{70}Mo_2N_8O_8$
Formula weight	1223.12
Temperature (K)	296.15
Crystal system	triclinic
Space group	*P*-1
a (Å)	10.1446(4)
b (Å)	10.3351(4)
c (Å)	13.9623(6)
α (°)	80.151(2)
β (°)	75.251(2)
γ (°)	82.226(2)
Volume (Å^3)	1388.3(1)

The ^{1}H NMR spectrum of $Mo_2(ArNC(H)NAr)_4$ exhibits two signals in the aromatic region, which is consistent with 4-fold symmetry. The solid-state structure (**Figure 7**) is consistent with the point group D_4 and features a short Mo–Mo bond (2.0925(3) Å). The atomic radii of Mo is 1.45 Å. Therefore, using equation 1, the FSR value for the M–M bond in $Mo_2(ArNC(H)NAr)_4$ is 0.72. This value is lower than that observed for the Mo–Mo quadruply bonded complex $Mo(hpp)_4$ (hpp = 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidinate), which has an FSR value of 0.797, and is consistent with the presence of a M–M quadruple bond.[3]

Commented [HK9]: In the NMR could you highlight this region or make a box around the peaks which indicate 4-fold symmetry?

yes

Commented [HK10]: Is this a typical value for quadruple bonds? What is a normal range for this type of bonds and when would you know that it is not a quadruple but a triple bond for example?

I don't think ranges can really be given here, since some quadruple bonds have higher FSR values than triple bonded compounds. I think it depends on the ligand assignment.

Summary:

In this video, we learned about M–M bonding. We synthesized a dinuclear molybdenum complex featuring a quadruple bond. Quadruple bonds consist of three different bond types, including σ, π, and δ bonds. We collected single crystal x-ray diffraction data and observed a short Mo–Mo bond length consistent with a quadruply bonded compound.

Applications:

Paddlewheel complexes, such as the Mo_2 complex prepared here, display a wide range of properties and thus find application in diverse areas of chemistry. For example, M–M bonds play an important role in catalysis: the dirhodium paddlewheel complex $Rh_2(OAc)_4$ is a known catalyst for C–H bond functionalization via carbene and nitrene transfer reactions (**Figure 9**). In a typical carbene transfer reaction, $Rh_2(OAc)_4$ reacts with a diazo compound to generate a Rh_2 carbene intermediate. Subsequent insertion of the carbene into a C–H bond generates the product of C–H functionalization and regenerates the $Rh_2(OAc)_4$ catalyst. The exceptional reactivity of Rh_2 catalysts in these reactions has been ascribed to Rh–Rh interaction via the M–M bond. The Rh–Rh bond in the resulting intermediate acts as an electron reservoir; while one metal serves as a binding site for substrate, the second metal center shuttles electron density to and from the active metal center during substrate activation. The *d*-orbital splitting diagram of the intermediate complex (Rh–Rh core bound to the carbenoid) shows that the frontier *d*-orbitals are non-bonding with respect to the active Rh center (**Figure 8a**). The electron density in both the σ and π non-bonding MOs is centered on the nucleophilic carbenoid carbon and the “spectator” Rh center, which is not directly bound to the carbenoid unit (**Figure 8b**).[4]

Paddlewheel complexes have also been utilized as building blocks in MOFs. MOFs are porous coordination polymers that consist of metal complexes linked together by organic ligands. The resulting one-, two-, or three-dimensional superstructures can be used in a variety of applications ranging from gas absorption (including separation and purification) to catalysis.

Legend:

Figure 1. General structure of paddlewheel complexes, where M can be a 1st, 2nd, or 3rd row transition metal.

Figure 2. Visual representation of σ, π, and δ bonding MOs resulting from the linear combination of metal *d*-orbitals. The d_{z^2} atomic orbitals have the best spatial overlap, followed by the d_{xz} and d_{yz} orbitals. The d_{xy} atomic orbitals have the least amount of spatial overlap.

Figure 3. Defined axes for the molecule $Mo_2(ArNC(H)NAr)_4$, assuming highest symmetry (D_{4h}).

Figure 4. MO diagram of the M–M bonding in $Mo_2(ArNC(H)NAr)_4$.

Figure 5. Synthesis of ArN(H)C(H)NAr, where Ar = *p*-$MeOC_6H_4$.

Figure 6. Synthesis of $Mo_2(ArNC(H)NAr)_4$, where Ar = *p*-$MeOC_6H_4$.

Figure 7. Solid-state structure for $Mo_2(ArNC(H)NAr)_4$ with the thermal ellipsoids set at the 50% probability level. Hydrogen atoms are omitted for clarity (Mo navy, N blue, C gray).

Figure 9. C–H bond functionalization via a metal-carbenoid intermediate.

Figure 8. (a) *d*-orbital MO splitting diagram of the Rh-Rh core in paddlewheel complexes bound to a carbenoid substrate. Note that only orbitals involved in substrate binding are shown. **(b)** The resulting σ and π non-bonding MOs are filled with electrons. The electron density in those MOs is centered on the carbenoid carbon and the "spectator" Rh center.

References

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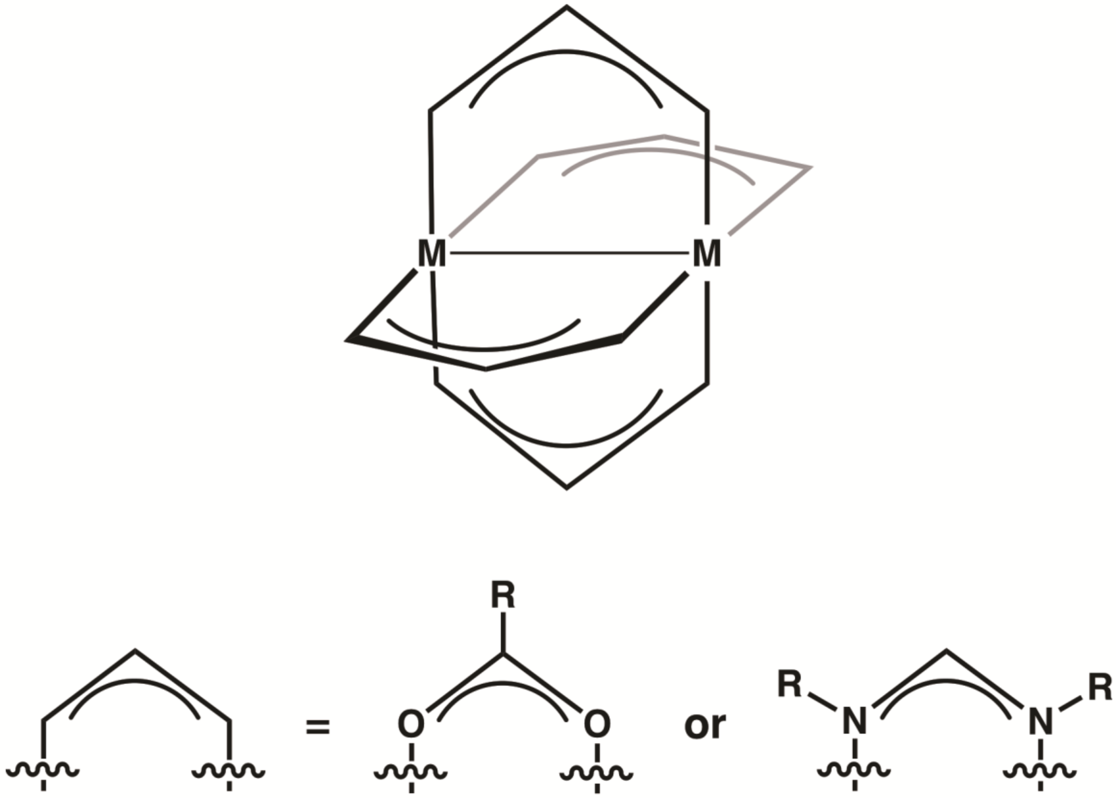


Figure 1.

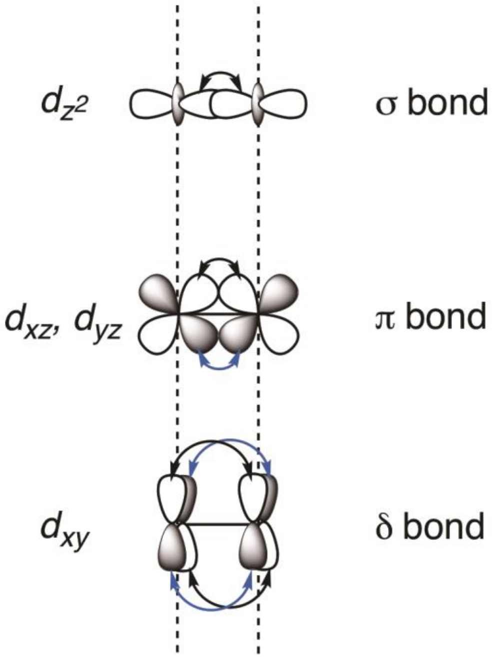


Figure 2.

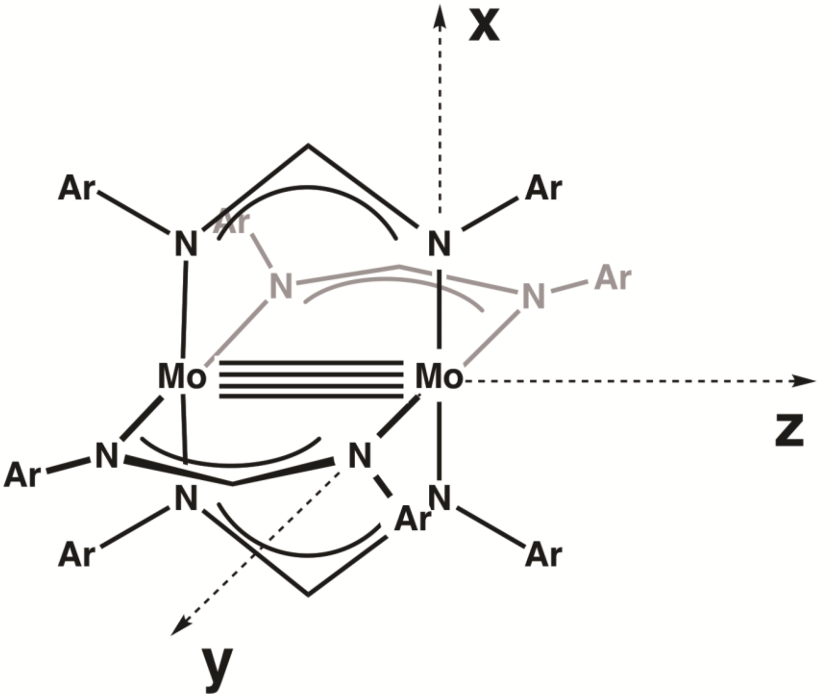


Figure 3.

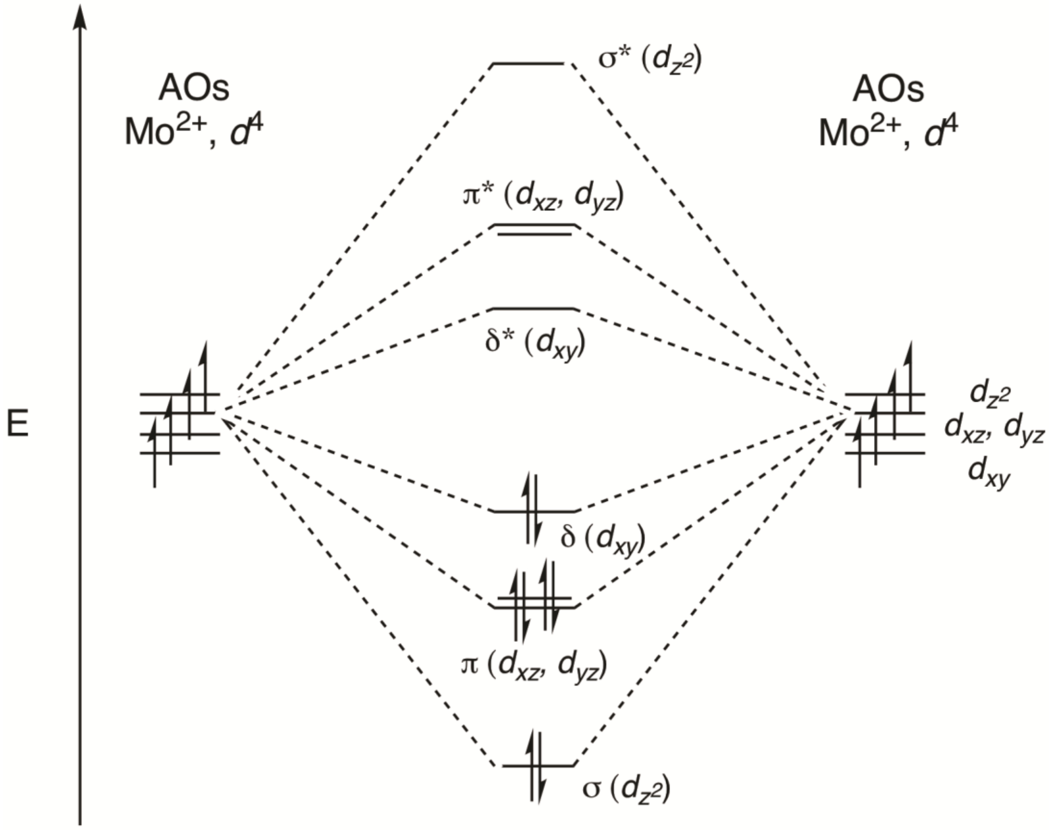


Figure 4.

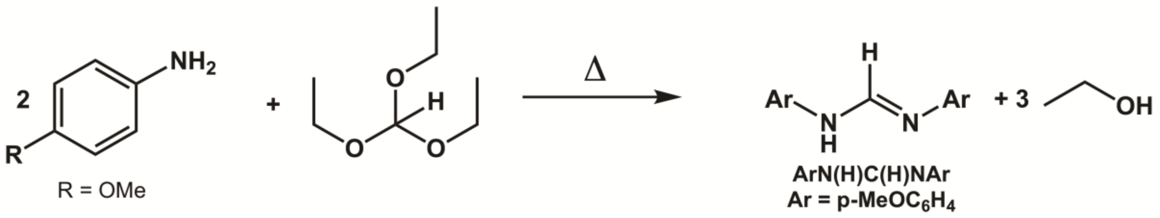
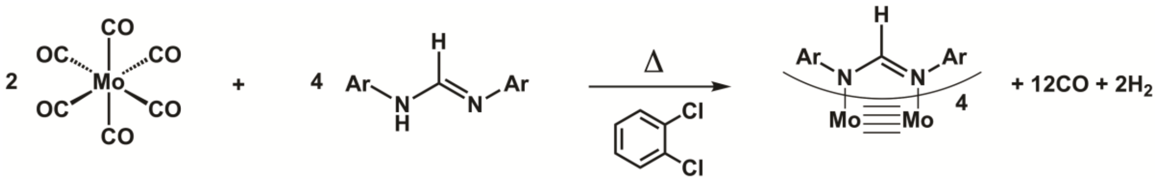


Figure 5.



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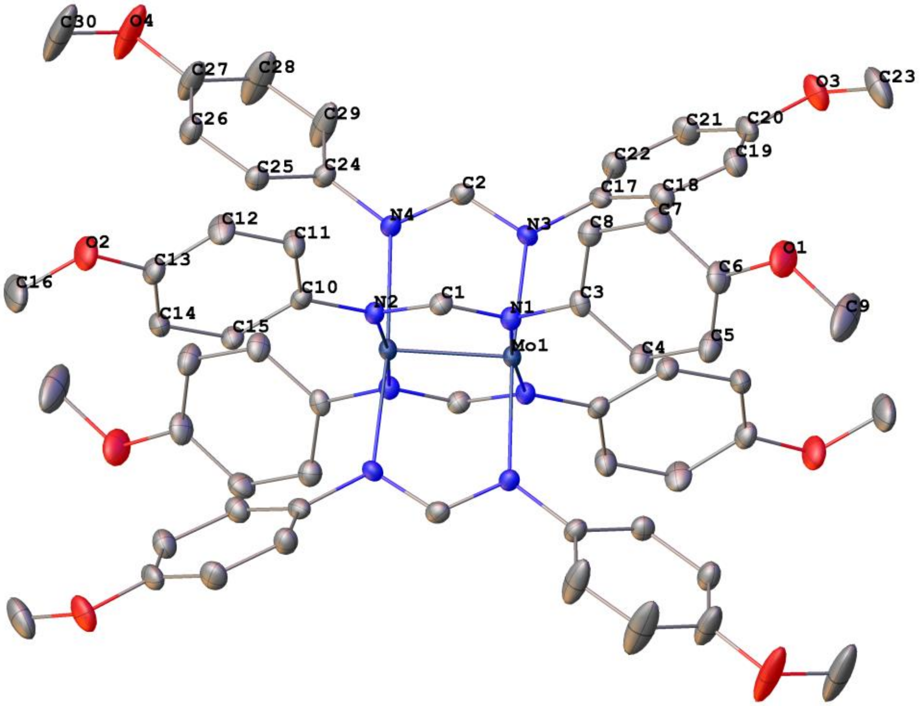

Figure 7.

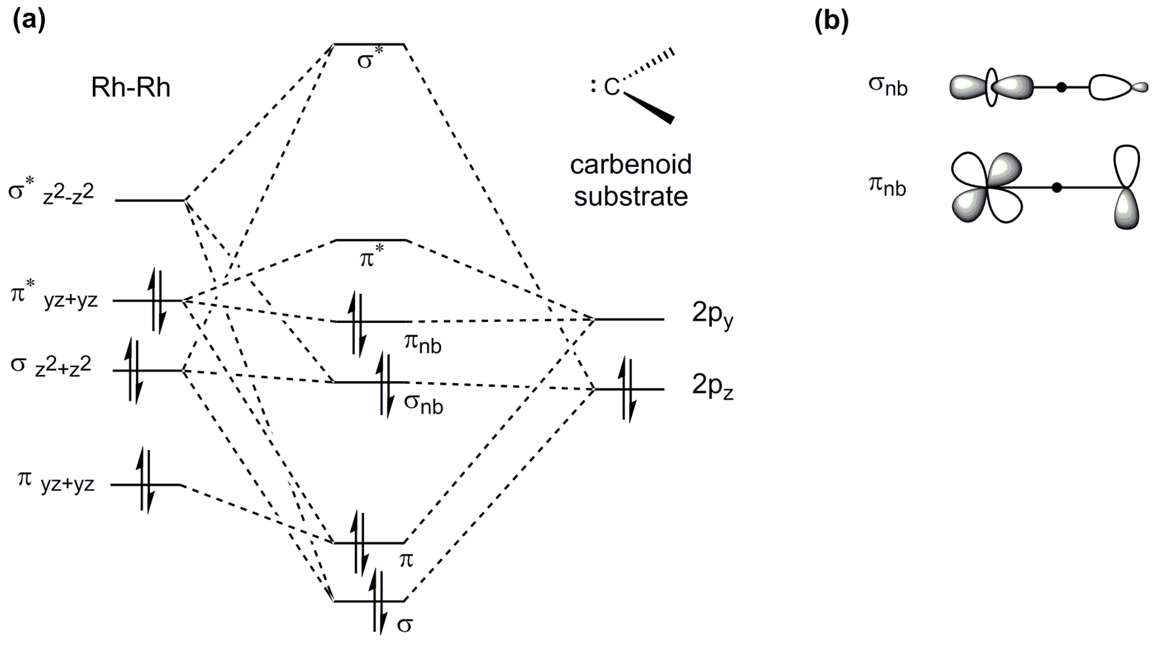

Figure 8.

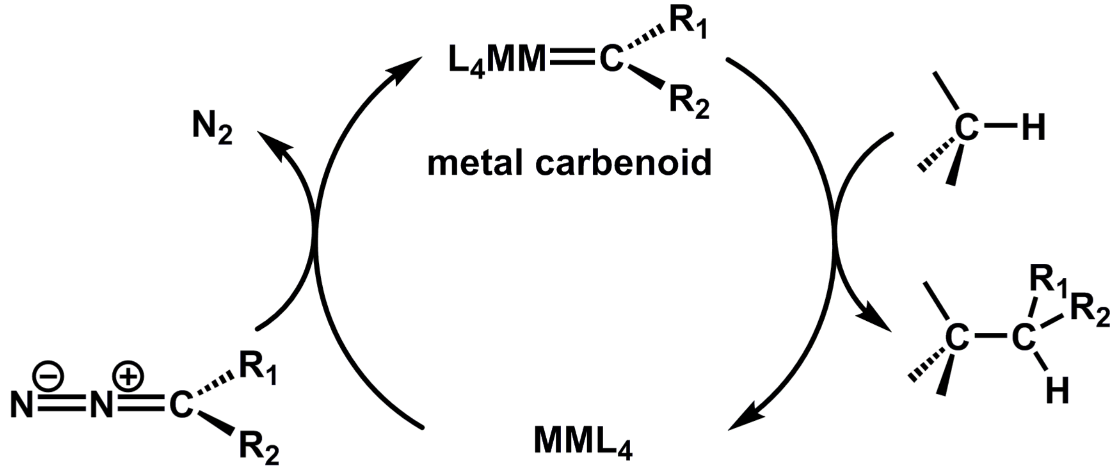

Figure 9.