REACTIVITY OF A NUCLEOPHILIC PYRAMIDAL PHOSPHINIDENE COMPLEX WITH ORGANIC AZIDES

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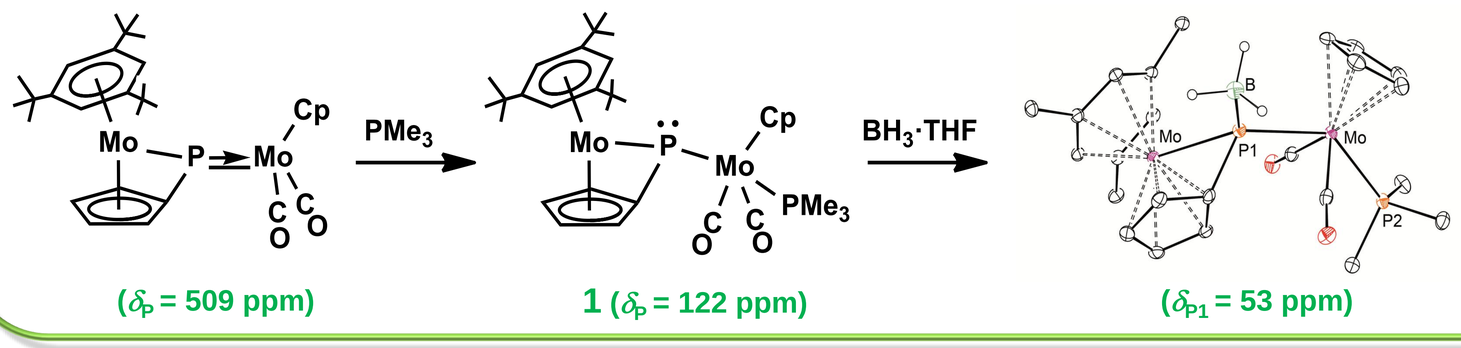
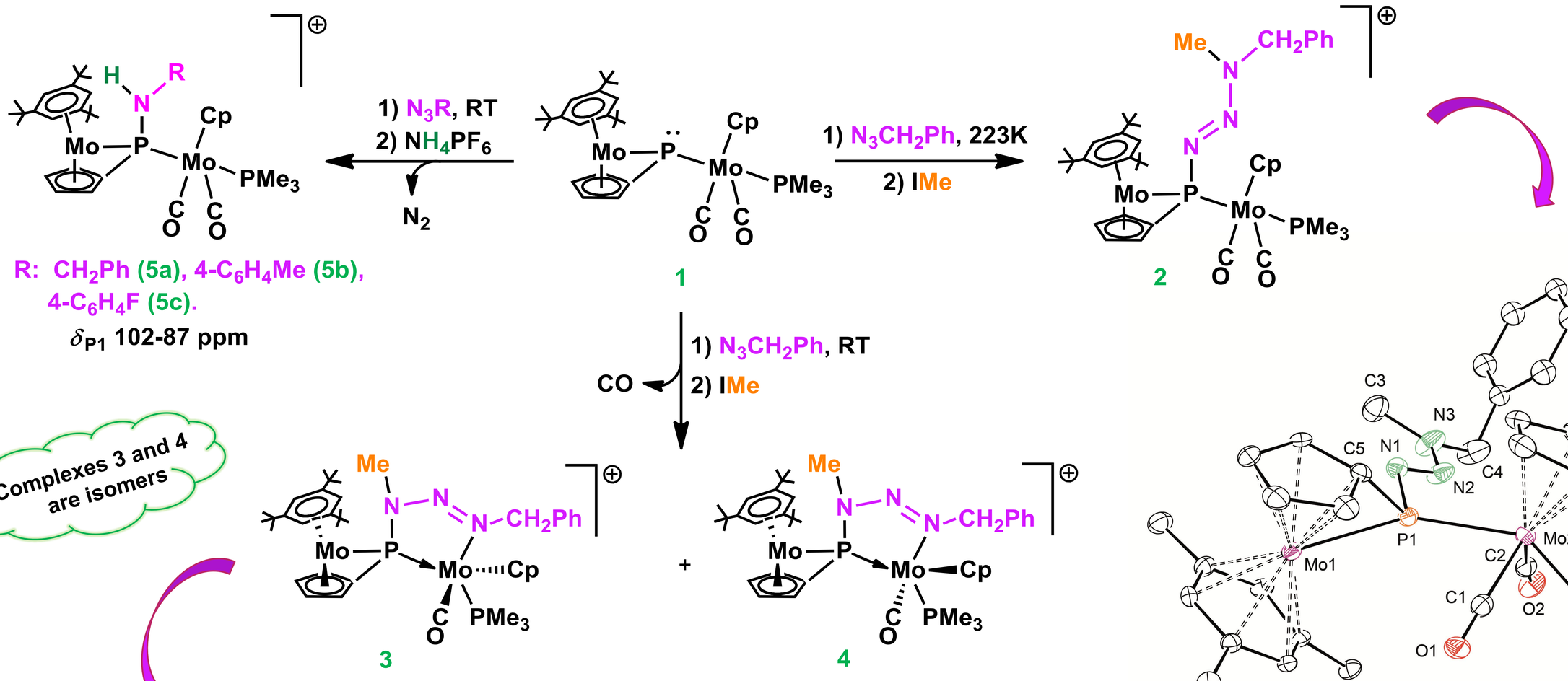
The study of formation and reactivity of phosphinidene complexes is a very active area of current research in Organometallic Chemistry, mainly because these species are useful precursors for a great variety of organophosphorus derivatives.[1] Reactions of phosphinidene complexes with organic azides are interesting in the context of formation of P-N bonds and the Staudinger reaction, and they can yield coordinated phosphatriazadiene ligands (RPN_3R'), iminophosphinidene ligands and even N_3P four-membered triazaphosphete complexes.[2]

In order to analyze the influence of ligand environment in these reactions, we have synthesized and studied the chemical behaviour of complex $[Mo_2Cp(\mu\text{-}\kappa^1\text{:}\kappa^1,\eta^5\text{-}PC_5H_4)(\eta^6\text{-}HMes^*)(CO)_2(PMe_3)]$ (1), where the ligand adopts a pyramidal arrangement.



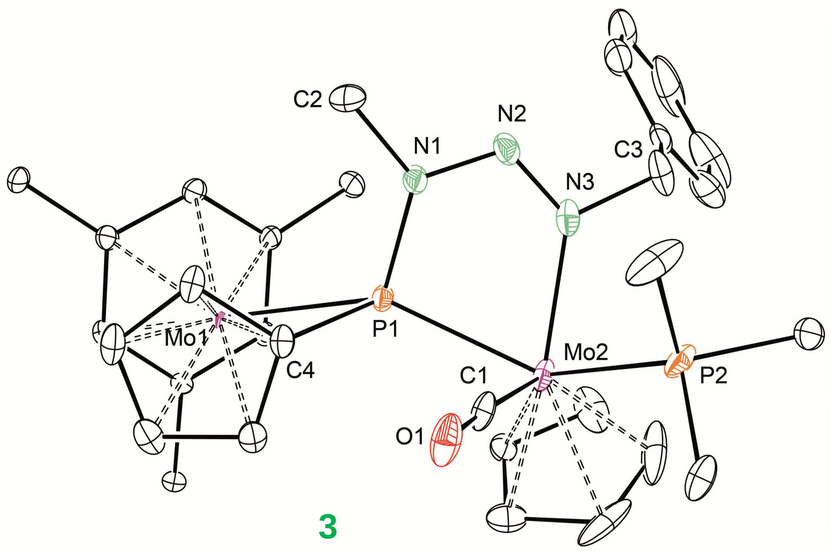
(δ_P = 509 ppm) — 1 (δ_P = 122 ppm) — (δ_{P1} = 53 ppm)

Complex 1 is readily obtained from the reaction of $[Mo_2Cp(\mu\text{-}\kappa^1\text{:}\kappa^1,\eta^5\text{-}PC_5H_4)(\eta^6\text{-}HMes^*)(CO)_2]$ with PMe_3, and its basicity is proven by its rapid reaction with BH_3·THF to give the borane adduct $[Mo_2Cp\{\mu\text{-}\kappa^1\text{:}\kappa^1,\eta^5\text{-}(BH_3)PC_5H_4\}(\eta^6\text{-}HMes^*)(CO)_2(PMe_3)]$.[3]



R: CH_2Ph (5a), 4-C_6H_4Me (5b), 4-C_6H_4F (5c).
δ_{P1} 102-87 ppm

δ_{P1} 224.8 ppm



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Compound 3

I.R. (CH_2Cl_2): ν(CO): 1850 (s) cm^{-1}
δ_{P1} 227.7 ppm, δ_{P2} 13.3 ppm [J_{PP} = 35 Hz]

Distances (Å):

P1–N1	1.749(4)	N1–C2	1.467(6)
N1–N2	1.335(5)	P1–C4	1.782(4)
N2–N3	1.288(5)	P1–Mo1	2.445(1)
N3–C3	1.494(6)	P1–Mo2	2.505(1)
Mo1–N3	2.184(4)	O1–C1	1.171(6)

Compound 2

I.R. (CH_2Cl_2): ν(CO): 1963 (w), 1885 (s) cm^{-1}
δ_{P1} 124.3 ppm, δ_{P2} 20.2 ppm [J_{PP} = 24 Hz]

Distances (Å):

P1–N1	1.737(5)	O1–C1	1.154(7)
N1–N2	1.262(8)	O2–C2	1.143(8)
N2–N3	1.313(8)	P1–Mo1	2.551(1)
N3–C3	1.439(10)	P1–Mo2	2.508(1)
N3–C4	1.459(9)	P1–C5	1.784(6)

These reactions proceed through unstable zwitterionic intermediates that can be trapped upon protonation or methylation of the initial reaction mixtures. A variety of compounds can be thus generated depending on reaction conditions, following from additional processes such as decarbonylation, loss of N_2 and intramolecular cyclization.

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References

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