Phosphorus–carbon bond activation of PMe₃ at a dimolybdenum center: synthesis and structure of [Cp*Mo(μ-O₂CMe)]₂(μ-PMe₂)(μ-Me)

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The reaction of $Mo_2(\mu\text{-}O_2CMe)_4$ with KCp* in the presence of PMe_3 yields $[Cp*Mo(\mu\text{-}O_2CMe)]_2(\mu\text{-}PMe_2)(\mu\text{-}Me)$ as a result of cleavage of the P–CH₃ bond.

The quadruply bonded dimolybdenum acetato complex $Mo_2(\mu\text{-}O_2CMe)_4$ has been shown to exhibit an extensive chemistry, allowing access to a large variety of mononuclear, dinuclear and polynuclear complexes.[1] In this paper, we report an unusual reaction of $Mo_2(\mu\text{-}O_2CMe)_4$ which results in P–C bond activation of PMe₃ at a dimolybdenum center.

As part of an effort to find new methods of synthesis for permethylcyclopentadienyl molybdenum complexes,[2] we have studied the reaction of $Mo_2(\mu\text{-}O_2CMe)_4$ with KCp* (Cp* = η^5-C₅Me₅) in the presence of PMe₃. Interestingly, rather than yielding a 'molybdenocene' derivative,[3] the bridging dimethylphosphido–methyl complex, $[Cp*Mo(\mu\text{-}O_2CMe)]_2(\mu\text{-}PMe_2)(\mu\text{-}Me)$, is obtained in *ca.* 30% isolated yield over a period of 3 days at room temperature (Scheme 1). The molecular structure of $[Cp*Mo(\mu\text{-}O_2CMe)]_2(\mu\text{-}PMe_2)(\mu\text{-}Me)$ has been determined by X-ray diffraction (Fig. 1 and Table 1),[4] thereby demonstrating that the P–CH₃ bond of PMe₃ has been cleaved. ¹H and ¹³C NMR spectroscopic data also provide decisive evidence in accord with this formulation. For example, the ¹H NMR spectrum exhibits three doublets at δ 0.97 ($^2J_{PH}$ 10 Hz), 0.91 ($^2J_{PH}$ 9 Hz), and −5.25 ($^3J_{PH}$ 5 Hz) for the [Mo₂(μ-PMe₂)(μ-Me)] moiety, with the lattermost resonance attributed to the molybdenum methyl group.
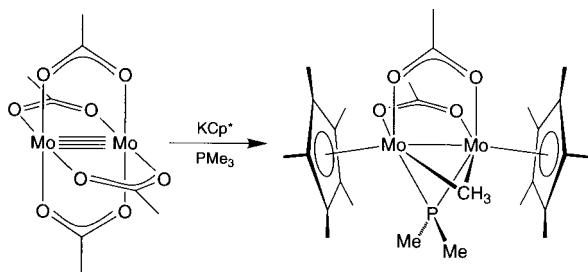

Scheme 1
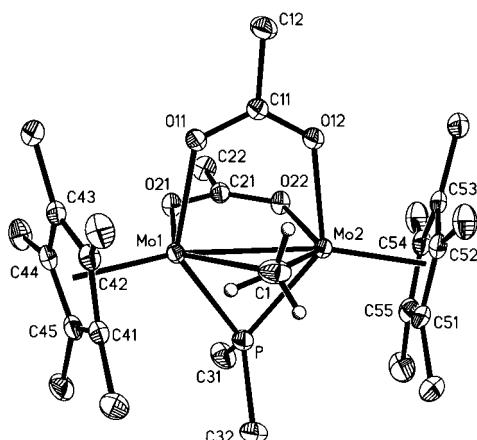
Fig. 1 Molecular structure of [Cp*Mo(μ-O₂CMe)]₂(μ-PMe₂)(μ-Me)

Table 1 Selected bond lengths for [Cp*Mo(μ-O₂CMe)]₂(μ-PMe₂)(μ-Me)

X	$d[Mo(1)\text{–}X]^a$/Å	$d[Mo(2)\text{–}X]^b$/Å
Mo(x)	2.8447(5)	2.8447(5)
C(1)	2.300(7)	2.301(7)
P	2.3883(13)	2.3853(13)
O(1y)	2.179(3)	2.161(3)
O(2y)	2.145(3)	2.152(3)
C(z1)	2.259(4)	2.251(5)
C(z2)	2.241(4)	2.253(4)
C(z3)	2.364(4)	2.371(4)
C(z4)	2.419(4)	2.421(5)
C(z5)	2.352(4)	2.327(5)

^{a} $x = 2, y = 1, z = 4$. ^{b} $x = 1, y = 2, z = 5$.

The facile cleavage of the P–CH₃ bond in the formation of $[Cp*Mo(\mu\text{-}O_2CMe)]_2(\mu\text{-}PMe_2)(\mu\text{-}Me)$ is of interest not only because such transformations are rare,[5,6] but also because the P–CH₃ bond cleavage in this system takes precedence over the much more ubiquitous C–H bond cleavage reactions of PMe₃.[7] Furthermore, the structure of $[Cp*Mo(\mu\text{-}O_2CMe)]_2(\mu\text{-}PMe_2)(\mu\text{-}Me)$ is noteworthy because both [PMe₂] and [Me] fragments remain coordinated to the metal centers after cleavage has taken place. We are aware of three other examples of P–CH₃ cleavage reactions of PMe₃,[8–10] only one of which yields a product that contains both [PMe₂] and [Me] groups coordinated to a metal, namely the reaction of CpNi(μ-H)(μ-CO)WCp₂ with PMe₃ to give CpNi(μ-PMe₂)(μ-CO)W-CpMe(PMe₃).[8]

In addition to representing a noteworthy example of P–C bond cleavage, [Cp*Mo(μ-O₂CMe)]₂(μ-PMe₂)(μ-Me) is also of interest from a structural perspective since there are no examples of dimolybdenum complexes with bridging methyl groups listed in the Cambridge Structural Database.[11,12] Bridging methyl groups have been proposed to adopt five different coordination modes (Scheme 2), which may be classified as (i) symmetric pyramidal,[13] (ii) symmetric planar,[14] (iii) monohapto agostic,[15] (iv) dihapto agostic,[16,17] and (v) trihapto agostic.[17,18] Of these modes, the bridging methyl group in [Cp*Mo(μ-O₂CMe)]₂(μ-PMe₂)(μ-Me) is appropriately described as symmetric pyramidal, with chemically equivalent Mo–C bond lengths [2.300(7) and 2.301(7) Å][19] and an acute Mo–C–Mo bond angle [76.4(2)°].[20] The $^1J_{CH}$ coupling constant associated with this methyl group is 113 Hz, less than that for
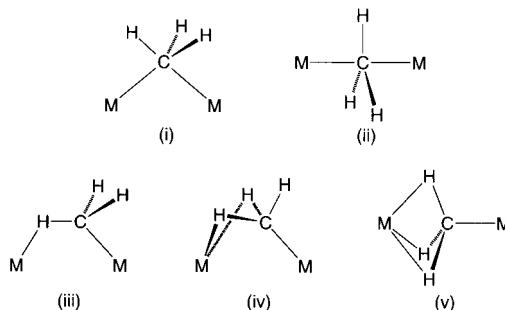
Scheme 2

typical terminal molybdenum methyl groups (*ca.* 127–136 Hz),[21] and possibly reflects a diminished s-contribution to the C–H bond,[22] rather than an agostic interaction.[20]

The Mo–Mo separation of 2.8447(5) Å in [Cp*Mo(μ-O$_2$CMe)]$_2$(μ-PMe$_2$)(μ-Me) is consistent with the presence of a direct Mo–Mo interaction.[23] In this regard, the Mo–Mo separation is longer than the values in complexes with formal double bonds, *e.g.* [CpMo]$_2$(μ-S)$_2$(μ-SPr^i)(μ-PPh$_2$) [2.623(2) Å][24] and [(C$_5$Me$_4$H)Mo(CO)](μ-PPh$_2$)$_2$[Mo(CO)(C$_5$Me$_4$-P(O)Ph$_2$)] [2.744(1) Å],[25] and notably shorter than the values in other phosphido bridged complexes such as [CpMo(CO)$_2$]$_2$(μ-PMe$_2$)(μ-H) [3.262(7) Å],[26] [CpMo(CO)$_2$]$_2$(μ-PBu^t)(μ-H) [3.247(1) Å],[27] and [CpMo(CO)$_2$]$_2$(μ-PPh$_2$)(μ-H) [3.244(1) Å].[28,29] Furthermore, the length of the Mo–Mo bond in [Cp*Mo(μ-O$_2$CMe)]$_2$(μ-PMe$_2$)(μ-Me) is marginally longer than the W–W separation of 2.78 Å in Chisholm's closely related tungsten complex, Cp$_2$W$_2$(μ-η^2-O$_2$CEt)$_2$(μ-η^1-O$_2$CEt)(μ-NMe$_2$), which has been assigned to a single bond.[30]

In summary, the reaction of Mo$_2$(μ-O$_2$CMe)$_4$ with KCp* in the presence of PMe$_3$ yields [Cp*Mo(μ-O$_2$CMe)]$_2$(μ-PMe$_2$)(μ-Me), the formation of which involves a novel P–CH$_3$ cleavage reaction of PMe$_3$.

Notes and References

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1 *Multiple Bonds Between Metal Atoms*, ed. F. A. Cotton and R. A. Walton, Clarendon Press, Oxford, 2nd edn., 1993.
2 See, for example: J. H. Shin and G. Parkin, *Polyhedron*, 1994, **13**, 1489.
3 For example, Mo$_2$(μ-O$_2$CMe)$_4$ reacts with NaCp to yield 'molybdenocene' derivatives.[3a,b] Furthermore, a pentalene complex has been obtained from the reaction of Mo$_2$(μ-O$_2$CMe)$_4$ with K$_2$[C$_8$H$_4$(1,4-SiPr^i$_3$)$_2$].[3c] (*a*) J. C. Smart and C. J. Curtis, *Inorg. Chem.*, 1978, **17**, 3290; (*b*) J. Bashkin, M. L. H. Green, M. L. Poveda and K. Prout, *J. Chem. Soc., Dalton Trans.*, 1982, 2485; (*c*) M. C. Kuchta, F. G. N. Cloke and P. B. Hitchcock, *Organometallics*, 1998, **17**, 934.
4 [Cp*Mo(μ-O$_2$CMe)]$_2$(μ-PMe$_2$)(μ-Me) is monoclinic, *P*2$_1$/*n* (no. 14), *a* = 10.989(1), *b* = 14.0436(9), *c* = 18.844(2) Å, *β* = 90.353(9)°, *U* = 2908(1) Å^3, *Z* = 4, *T* = room temp., *R$_1$* = 0.0404 [*I* > 2σ(*I*)]. The hydrogen atoms of the bridging methyl group were located and refined isotropically, giving the following bond lengths (Å): C1–H1a 0.86, C1–H1b 0.97, C1–H1c 0.84 Å. CCDC 182/868.
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6 In contrast to P–C cleavage in alkylphosphines, the cleavage of P–C bonds in arylphosphines is common, with the ease of cleavage typically following the order P–C$_{sp3}$ < P–C$_{sp2}$ < P–C$_{sp}$.[5] The majority of examples of P–C$_{sp3}$ bond cleavage, however, involve degradation of bidentate phosphine ligands.[6a–e] (*a*) V. Riere, M. A. Ruiz, F. Villafañe, C. Bois and Y. Jeannin, *J. Organomet. Chem.*, 1989, **375**, C23; (*b*) I. J. B. Lin, J. S. Lai and C. W. Liu, *Organometallics*, 1990, **9**, 530; (*c*) K.-B. Shiu, S.-W. Jean, H.-J. Wang, S.-L. Wang, F.-L. Liao, J.-C. Wang and L.-S. Liou, *Organometallics*, 1997, **16**, 114 and references therein; (*d*) N. M. Doherty, G. Hogarth, S. A. R. Knox, K. A. Macpherson, F. Melchior, D. A. V. Morton and A. G. Orpen, *Inorg. Chim. Acta*, 1992, **198–200**, 257; (*e*) F. A. Cotton, J. A. M. Canich, R. L. Luck and K. Vidyasagar, *Organometallics*, 1991, **10**, 352.
7 See, for example: F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, 1988, 5th edn., p. 1217; A. D. Ryabov, *Chem. Rev.*, 1990, **90**, 403; A. E. Shilov and G. B. Shul'pin, *Chem. Rev.*, 1997, **97**, 2879.
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11 CSD Version 5.14. *3D Search and Research Using the Cambridge Structural Database*, F. H. Allen and O. Kennard, *Chem. Des. Automat. News*, 1993, **8**(1), 1 and 31.

12 It is also noteworthy that the Cp* ligands of [Cp*Mo(μ-O$_2$CMe)]$_2$(μ-PMe$_2$)(μ-Me) are not coordinated in a symmetric η^5-fashion, with Mo–C bond lengths that range from 2.24 to 2.42 Å (see Table 1).
13 Representative examples include [Me$_2$Al(μ-Me)]$_2$,[13a] [Cp*CrMe(μ-Me)]$_2$,[13b] {[Cp^R]$_2$M(μ-Me)}$_2$ (M = Ce, Yb, Y)[13c] and {Me$_3$Al-[(Me$_3$Si)$_2$N]Mn(μ-Me)}$_2$.[13d] (*a*) J. C. Huffman and W. E. Streib, *Chem. Commun.*, 1971, 911; (*b*) S. K. Noh, S. C. Sendlinger, C. Janiak and K. H. Theopold, *J. Am. Chem. Soc.*, 1989, **111**, 9127; (*c*) S. D. Stults, R. A. Andersen and A. Zalkin, *J. Organomet. Chem.*, 1993, **462**, 175 and references therein; (*d*) M. Niemeyer and P. P. Power, *Chem. Commun.*, 1996, 1573.
14 For example, [Cp$_2$Zr(η^2-OCMe$_2$)]$_2$(μ-AlMe$_2$)(μ-Me),[14a] Cp*$_2$Lu(μ-Me)LuMeCp*$_2$,[14b] Cp*$_2$M[(μ-Me)M'Me$_2$(μ-Me)]$_2$MCp*$_2$ (M = Y, Lu; M' = Al, Ga),[14c] Cp*$_2$Sm[(μ-Me)AlMe$_2$(μ-Me)]$_2$SmCp*$_2$[14d] and [(Cp^{Me})$_3$U]$_2$(μ-Me).[14e] (*a*) R. W. Waymouth, K. S. Potter, W. P. Schaefer and R. H. Grubbs, *Organometallics*, 1990, **9**, 2843 and references therein; (*b*) P. L. Watson, *J. Am. Chem. Soc.*, 1983, **105**, 6491; (*c*) M. A. Busch, R. Harlow and P. L. Watson, *Inorg. Chim. Acta*, 1987, **140**, 15; (*d*) W. J. Evans, L. R. Chamberlain, T. A. Ulibarri and J. W. Ziller, *J. Am. Chem. Soc.*, 1988, **110**, 6423; (*e*) S. D. Stults, R. A. Andersen and A. Zalkin, *J. Am. Chem. Soc.*, 1989, **111**, 4507 and references therein.
15 For examples, and for a discussion of the factors responsible for the bridging methyl group in [{Cp(CO)Fe}$_2$(μ-CO)(μ-Me)]$^+$ adopting a monohapto agostic interaction, see: B. E. Bursten and R. H. Cayton, *Organometallics*, 1986, **5**, 1051 and references therein.
16 For example, Cp*$_2$Yb(μ-Me)$_2$Pt(dippe)[16a] and [CpV(NC$_6$H$_3$Pr^i$_2$)(μ-Me)$_2$]$_2$(μ-Mg).[16b] (*a*) D. J. Schwartz, G. E. Ball and R. A. Andersen, *J. Am. Chem. Soc.*, 1995, **117**, 6027; (*b*) M. C. W. Chan, J. M. Cole, V. C. Gibson and J. A. K. Howard, *Chem. Commun.*, 1997, 2345.
17 [LiBMe$_4$] exhibits both dihapto and trihapto bridging methyl interactions. See: W. E. Rhine, G. Stucky and S. W. Peterson, *J. Am. Chem. Soc.*, 1975, **97**, 6401.
18 For example, Cp*$_2$Yb(μ-Me)BeCp*. See: C. J. Burns and R. A. Andersen, *J. Am. Chem. Soc.*, 1987, **109**, 5853.
19 For comparison, the mean length for terminal Mo–CH$_3$ interactions listed in the Cambridge Structural Database is 2.23 Å, with a range of 2.03–2.40 Å.
20 Although a short Mo···H separation of 2.02 Å suggests that some monohapto agostic character to the interaction could be considered, we feel that the equivalence of the Mo–C bond lengths and the acute Mo–C–Mo bond angle is a more important indicator of the type of bridge [see, for example ref. 13(*c*)].
21 For example, (Cp$^{Bu^t}$)$_2$MoMe$_2$ (128 Hz),[21a] [(Cp$^{Bu^t}$)$_2$Mo(CO)Me][I] (136 Hz),[21a] [(Cp$^{Bu^t}$)$_2$Mo(PMe$_3$)Me][I] (130 Hz),[21a] and Cp*Mo-(NO)$_2$Me (127 Hz).[21b] (*a*) J. H. Shin and G. Parkin, unpublished work; (*b*) W. L. Elcesser, M. Sörlie and J. L. Hubbard, *Organometallics*, 1996, **15**, 2534.
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23 Considering a bridging methyl group as a L–μ-X ligand,[23a] the Mo–Mo interaction may be described as a formal single bond. Alternatively, the interaction may be described as a formal double bond if an electron counting procedure[23b] that does not explicitly consider the 3-center–2-electron nature of the Mo–Me–Mo fragment is used. (*a*) M. L. H. Green, *J. Organomet. Chem.*, 1995, **500**, 127; (*b*) J. P. Collman, L. S. Hegedus, J. R. Norton and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987.
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29 For further comparison, the unbridged Mo–Mo single bond length in [CpMo(CO)$_3$]$_2$ is 3.235(1) Å. See: R. D. Adams, D. M. Collins and F. A. Cotton, *Inorg. Chem.*, 1974, **13**, 1086.
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