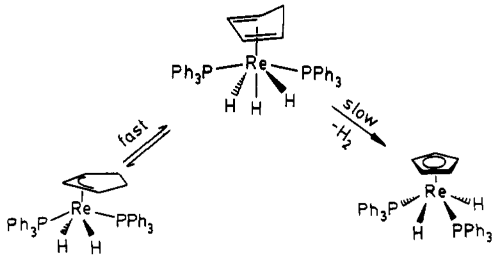
volves rotation of the η^4-C_5H_6 group. The hydride exchange can be accounted for as a pairwise exchange that might only occur with the cyclopentadiene rotated 90° from its most stable orientation.

A third fluxional process shows broadening of both the hydride ligands and the four C_5H_6 resonances beginning at ~50 °C. Complete collapse of the C_5H_6 resonances occurs at 80 °C as a resonance begins to grow in at δ 3.57. At 90 °C the hydride resonance disappears into the base line, but decomposition to form **3** occurs rapidly at this temperature before the limiting high-temperature spectrum can be attained.

The nature of this process is revealed by irradiating the hydride resonance at δ −5.67 at temperatures above 40 °C and observing the complete collapse of only the C_5H_6 resonance at δ 3.353. This latter resonance can be confidently assigned to the endo hydrogen of the η^4-C_5H_6 group, which apparently undergoes exchange with the hydride ligands on the time scale of relaxation processes (~1–5 s^{-1}). This corresponds to a ΔG^{*} of about 18.5 kcal/mol and is clearly a separate process from the other exchanges. In the fast-exchange limit, resonances would have been expected at δ 3.82 (5 H) and −3.30 (4 H).

While the exact nature of the latter exchange process is not known, a mechanism involving reversible reductive elimination of H_2 followed by migration of the endo η^4-C_5H_6 hydrogen to the metal can be ruled out since the formation of **3** is observed to be irreversible, even under 1000 psi of H_2. Reversible loss of phosphine followed by endo-hydrogen migration would produce $CpRe(PPh_3)H_4$, which does not react with PPh_3.[13] One possibility is shown in eq 2, involving reversible migration of a hydride ligand



(2)

to the C_5H_6 ring to form a symmetrical η^3-allyl intermediate. Such reversible migrations have been observed in the related η^4-cyclohexadiene system, which was also characterized structurally,[14] and in the related bis(ethylene) derivative.[8] Bercaw has also used a reversible metal to Cp ring hydrogen migration to account for H/D exchange in zirconium hydride complexes.[15] Further studies of this and related processes are under way.[16]

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Supplementary Material Available: Tables of data collection parameters, positional and thermal parameters, least-squares planes, bond angles and distances, and tables of structure factors (43 pages). Ordering information is given on any current masthead page.

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Simple Routes to Mono(η^5-pentamethylcyclopentadienyl) Complexes of Molybdenum(V) and Tungsten(V)

Robert Clark Murray, Lauren Blum, Andy H. Liu, and Richard R. Schrock*

Department of Chemistry, 6-331
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received July 13, 1984

Summary: Addition of $W(\eta^5$-$C_5Me_5)(CO)_3Me$ to PCl_5 in dichloromethane produces sparingly soluble $W(\eta^5$-$C_5Me_5)Cl_4$ as a bright orange powder in ~80% yield. $[NEt_4][W(\eta^5$-$C_5Me_5)Cl_5]$ and $W(\eta^5$-$C_5Me_5)Cl_4(PMe_3)$ can be prepared readily. Addition of excess $ZnMe_2$ to $W(\eta^5$-$C_5Me_5)Cl_4(PMe_3)$ produces yellow $W(\eta^5$-$C_5Me_5)Me_4$ in good yield. The reaction between $Mo(\eta^5$-$C_5Me_5)(CO)_3Me$ and PCl_5 in dichloromethane produces purple $Mo(\eta^5$-$C_5Me_5)Cl_4$. Addition of PMe_3 yields $Mo(\eta^5$-$C_5Me_5)Cl_4(PMe_3)$, but attempted preparations of $Mo(\eta^5$-$C_5Me_5)Me_4$ so far have failed. PCl_5 has also been used to prepare $W(\eta^5$-$C_5Et_5)Cl_4$ from $W(\eta^5$-$C_5Et_5)(O)Cl_3$.

The discovery of $[Ta(\eta^5$-$C_5Me_4R)(\mu$-$H)Cl_2]_2$ (R = Me, Et) complexes[1] and their reaction with carbon monoxide to give μ-hydride μ-formyl complexes of the type $[Ta(\eta^5$-$C_5Me_4R)Cl_2]_2(\mu$-$H)(\mu$-$CHO)$[2] led to a search for related chemistry of the less oxophilic metals Mo and W. Unfortunately, suitable high oxidation state mono(η^5-C_5Me_4R) starting materials such as $M(\eta^5$-$C_5Me_5)Cl_4$ were unknown. A tungsten complex with the formula $[W(\eta^5$-C_5Me_4-*t*-$Bu)Cl_4]_2$ was prepared via a reaction between the tungstenacyclobutadiene complex $W[C(t$-$Bu)C(Me)C(Me)]Cl_3$ and 2-butyne,[3] but a more direct route to analogous, simpler, η^5-C_5Me_5 complexes was clearly needed before the chemistry could be explored in detail. We report here simple, high-yield routes to molybdenum and tungsten complexes of the type $M(\eta^5$-$C_5Me_5)Cl_4$ (M = Mo, W).

All attempts to prepare $M(\eta^5$-$C_5Me_5)Cl_4$ complexes directly from MCl_x (x = 5 or 6) and a mild η^5-C_5Me_5 source such as $SnBu_3(C_5Me_5)$, a type of reaction that has yielded complexes such as $Ta(\eta^5$-$C_5Me_5)Cl_4$,[4] so far have failed. Therefore we chose to prepare a lower oxidation state complex containing one η^5-C_5Me_5 ring and subsequently oxidize it. A solution of $W(\eta^5$-$C_5Me_5)(CO)_3Me$[5] dissolved in dichloromethane was added dropwise at 25 °C to 2.5 equiv of PCl_5 partially dissolved in dichloromethane. The PCl_5 dissolved as the solution rapidly changed color to orange and gas (presumably CO) evolved. After the mixture was refluxed overnight, an almost iridescent orange powder was filtered off and washed liberally with dichloromethane. It could be sublimed at 200 °C and <0.1 μm. Elemental analysis[6a] and subsequent reactions (vide

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(6) (a) Anal. Calcd for $WC_{10}H_{15}Cl_4$: C, 26.06; H, 3.28; Cl, 30.77. Found: C, 26.30; H, 3.38; Cl, 29.27. (b) Anal. Calcd for $WC_{18}H_{35}Cl_5N$: C, 34.50; H, 5.63; Cl, 28.29. Found: C, 34.85; H, 5.81; Cl, 27.68. (c) Anal. Calcd for $WC_{13}H_{24}Cl_4P$: C, 29.08; H, 4.51; Cl, 26.41. Found: C, 29.42; H, 4.48; Cl, 25.64.

infra) were sufficient to characterize the almost CH_2Cl_2 insoluble species as $W(\eta^5\text{-}C_5Me_5)Cl_4$ (yield ~80%). We presume that it is a dimer by analogy with $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)Cl_4]_2$,[3] and in accord with the compound's insolubility. $W(\eta^5\text{-}C_5Me_5)Cl_4$ will react readily with NEt_4Cl in dichloromethane to give brown, crystalline $[NEt_4][W(\eta^5\text{-}C_5Me_5)Cl_5]$[6b] and with PMe_3 to form toluene-soluble, green, crystalline $W(\eta^5\text{-}C_5Me_5)Cl_4(PMe_3)$.[6c] $W(\eta^5\text{-}C_5Me_5)Cl_4$ and its PMe_3 adduct have signals in their EPR spectra in dichloromethane at 25 °C at $g = 1.92$ and $g = 1.90$, respectively, with half-height widths of 50 and 64 G, respectively.

An analogous reaction between $Mo(\eta^5\text{-}C_5Me_5)(CO)_3Me$[7] and PCl_5 in dichloromethane yields a purple solution from which microcrystalline purple $Mo(\eta^5\text{-}C_5Me_5)Cl_4$ can be isolated in ≳90% yield.[8a] Chloride ion will not add to the metal to give a stable complex of the type $[Et_4N][Mo(\eta^5\text{-}C_5Me_5)Cl_5]$, but trimethylphosphine will add to give purple $Mo(\eta^5\text{-}C_5Me_5)Cl_4(PMe_3)$.[8b] EPR spectra of $Mo(\eta^5\text{-}C_5Me_5)Cl_4$ and $Mo(\eta^5\text{-}C_5Me_5)Cl_4(PMe_3)$ in THF at 25 °C show relatively narrow peaks (half-height width ≈ 7 G) at $g = 1.99$ and 1.97, respectively, with couplings of 39 and 45 G to ^{97}Mo ($S = {}^5/_2$) and ^{95}Mo ($S = {}^5/_2$) and of ~27 G to ^{31}P in the case of $Mo(\eta^5\text{-}C_5Me_5)Cl_4(PMe_3)$.

$W(\eta^5\text{-}C_5Me_5)Cl_4(PMe_3)$ reacts smoothly with excess dimethylzinc in toluene to give a yellow, crystalline, paramagnetic complex ($g \approx 2$ in pentane at 25 °C) in good yield (~80%) that analyzes as $W(\eta^5\text{-}C_5Me_5)Me_4$.[9] An X-ray structural study of $W(\eta^5\text{-}C_5Et_3Me_2)Me_4$[10] confirms that the formulation is correct, that the molecule is a monomer and that the geometry is square pyramidal. $W(\eta^5\text{-}C_5Me_5)Cl_4$ reacts similarly with dimethylzinc, but the yield of $W(\eta^5\text{-}C_5Me_5)Me_4$ is only ~40%. So far we have not been able to prepare $Mo(\eta^5\text{-}C_5Me_5)Me_4$ in a similar manner.

One of the main reasons for developing the $W(\eta^5\text{-}C_5Me_5)Cl_4$ and $W(\eta^5\text{-}C_5Me_5)Me_4$ chemistry was in order to prepare and structurally characterize what we expected to be more crystalline complexes analogous to $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)H_4]_2$ and $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)H_3]_3$.[11] $W(\eta^5\text{-}C_5Me_5)Me_4$ reacts with H_2 at 1000 psig in pentane to yield a mixture of two hydride complexes having signals at −0.34 ($J_{HW} = 33$ Hz) and −1.65 ppm (br), respectively (cf. −0.81 and −1.86 ppm for the $\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu$ species above). ^1H NMR spectra of poorly crystalline samples of $[W(\eta^5\text{-}C_5Me_5)H_4]_2$ (obtained in ~25% yield by selective crystallization from pentane) show the expected hydride signal and ^{183}W satellite intensities (cf. the $\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu$ derivative[11]). The peak at −1.65 ppm in the mixture is assigned to $[W(\eta^5\text{-}C_5Me_5)H_3]_3$, the broadening being due to the slowing of a fluxional process that interconverts all hydride ligands (cf. $[W(\eta^5\text{-}C_5Me_4\text{-}t\text{-}Bu)H_3]_3$[11]). These results suggest that the above approach to hydride complexes will be generally successful for peralkylated cyclopentadienyl complexes.

We have not yet seen any reactions in the literature in which a transition-metal complex is chlorinated by PCl_5 and therefore are curious as to whether this type of reaction might be more generally useful for preparing other mono($\eta^5\text{-}C_5Me_5$) complexes, e.g., $Re(\eta^5\text{-}C_5Me_5)Cl_4$. We also are now able to explore the chemistry of $M(\eta^5\text{-}C_5Me_5)Cl_4$ (M = Mo, W) in more detail, in particular with respect to formation of alkyl and hydrido complexes.

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(8) (a) A solution of $Mo(\eta^5\text{-}C_5Me_5)(CO)_3Me$ (10 g) dissolved in 40 mL of dichloromethane was added to 16 g of PCl_5 partially dissolved in 200 ml of dichloromethane. Gas evolved and the solution turned purple. The solution was refluxed for 12 h, cooled, and filtered to give ~10.5 g of the intensely purple, microcrystalline product (~95% yield). Anal. Calcd for $MoC_{10}H_{15}Cl_4$: C, 32.20; H, 4.06; Cl, 38.02. Found: C, 32.03; H, 3.96; Cl, 37.31. (b) Anal. Calcd for $MoC_{13}H_{24}Cl_4P$: C, 34.77; H, 5.40; Cl, 31.58. Found: C, 35.35; H, 5.45; Cl, 31.61.

(9) Anal. Calcd for $WC_{14}H_{27}$: C, 44.34; H, 7.18. Found: C, 44.01; H, 6.66; Cl, ≲0.5.

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Nickel–Nickel Dimers: The Synthesis and Novel Structure of $[Ni_2(\mu\text{-}CNMe)(CNMe)_3(PPh_2CH_2PPh_2)_2][PF_6]_2$

Dru L. DeLaet, Douglas R. Powell,[‡] and Clifford P. Kubiak*

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

Received December 17, 1984

Summary: Conproportionation of $[Ni^{II}(CNMe)_4][PF_6]_2$ with $Ni^0(CNMe)_4$ results in formation of the new binuclear Ni^I complex $[Ni^I{}_2(CNMe)_8][PF_6]_2$, **1**. Reaction of **1** with bis(diphenylphosphino)methane (dppm) yields the novel, asymmetrically bridged complex $[Ni_2(\mu\text{-}CNMe)(CNMe)_3(dppm)_2][PF_6]_2\cdot CH_2Cl_2$, **2**. The structure of **2** as a solid has been determined by X-ray diffraction. In solution, **2** is fluxional and variable-temperature $^{31}P\{^1H\}$ NMR studies indicate rapid interconversion of the asymmetric structure of **2** above −45 °C.

While there exists a rich organometallic and catalytic chemistry of nickel,[1] the chemistry of direct Ni–Ni bonds has received relatively little attention. In the course of our studies of the chemistry and photochemistry of the metal–metal bonds of binuclear Pd(I) and Pt(I) complexes,[2-6] we sought to examine the corresponding properties of bonds between Ni(I) ions. We report herein the synthesis of new binuclear nickel complexes which display a range of unusual Ni–Ni interactions. The unprecedented structure of a bis(diphenylphosphino)methane (dppm) bridged complex is also described as well as preliminary studies of its chemistry.

The new binuclear Ni(I) isocyanide complex $[Ni_2{}^I(CNMe)_8][PF_6]_2$, **1**, was prepared by conproportionation

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[‡] Address correspondence pertaining to crystallographic studies to this author.

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