Organometallics 1992, *11*, 3293–3301

Tungsten(IV) Alkyls and η^2-Acyls. CO Insertion and Ligand Substitution Reactions of the Tungsten Dication $CpW(CO)_2(NCMe)_2Me^{2+}$ and Related Complexes

Vidar Skagestad and Mats Tilset*

Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway

Received April 27, 1992

The tungsten(IV) dication $CpW(CO)_2(NCMe)_2Me^{2+}$, obtained from the 2-electron oxidation of $CpW(CO)_3Me$, serves as the precursor to a number of tungsten(IV) complexes via a series of CO insertion and substitution reactions. In acetonitrile, the dication undergoes smooth CO insertion ($\Delta H^{\ddagger} = 89.5 \pm 2.5$ kJ/mol, $\Delta S^{\ddagger} = -43.9 \pm 8.4$ J/(K·mol), $k(20\ ^\circ C) = 3.3 \times 10^{-6}\ s^{-1}$) and substitution to give the η^2-acetyl complex $CpW(NCMe)_3(\eta^2\text{-}COMe)^{2+}$. The oxidation of $CpW(CO)_3Et$ provides $CpW(CO)(NCMe)_2(\eta^2\text{-}COEt)^{2+}$ via the intermediacy of $CpW(CO)_2(NCMe)_2Et^{2+}$. $CpW(CO)(NCMe)_2(\eta^2\text{-}COEt)^{2+}$ in turn undergoes CO substitution to yield $CpW(NCMe)_3(\eta^2\text{-}COEt)^{2+}$. Analogous CO insertion reactions were not observed for the compounds $CpW(CO)_3(NCMe)Me^{2+}$ and $CpW(CO)_3(NCMe)Et^{2+}$. It appears that η^2-acyl formation is favored by sterically demanding migrating groups and by donor (MeCN vs CO) substituents. In acetonitrile-d_3, the two identical acetonitrile ligands (both cis relative to the acetyl) in $CpW(NCMe)_3(\eta^2\text{-}COMe)^{2+}$ undergo exchange with the solvent at a rate much slower than the unique acetonitrile group which is located trans relative to the acetyl ligand. In the presence of PPh_3, the exchange of the two identical acetonitrile groups is greatly accelerated, whereas the rate of exchange of the unique acetonitrile ligand is unaffected. Photolysis of $CpW(CO)_2(NCMe)_2Me^{2+}$ yields $CpW(NCMe)_4Me^{2+}$ with $CpW(CO)(NCMe)_3Me^{2+}$ as an observed intermediate. The latter undergoes thermal CO insertion to yield $CpW(NCMe)_3(\eta^2\text{-}COMe)^{2+}$. The oxidation chemistry of $CpW(CO)_2(PPh_3)Me$ and $Cp'W(CO)_3Me$ ($Cp' = \eta^5\text{-}C_5H_4Me$) has been found to parallel that of $CpW(CO)_3Me$.

Introduction

The carbon monoxide migratory insertion has gained a prominent position in organotransition-metal chemistry due to its involvement in numerous catalytic and stoichiometric processes that are of great practical and industrial importance.[1] Significant efforts have been made at elucidating the factors that influence the kinetics and thermodynamics of CO insertion reactions.[1,2] When a coordinatively saturated metal alkyl carbonyl complex undergoes CO insertion, a formally coordinatively unsaturated metal acyl species is generated as a crucial intermediate.[1a] It has been proposed that this intermediate may be stabilized by different means, including solvent or nucleophile coordination,[2a,3] η^2-acyl coordination,[1a,4] and agostic interactions of acyl group hydrogens[5] with the metal center.

The chemistry of η^2-acyl complexes[4] has been dominated by the early, especially group 4, transition elements and other oxophilic metals. However, a multitude of group 6 and later η^2-acyl complexes are also known.[6–9] A great number of these represent Mo(II) or W(II) species with the general formula $L_4MX(\eta^2\text{-}COR)$ (L = 2-electron donor; X = halide or other 1-electron donor).[5,6] Only a few group 6 metal η^2-acyl complexes containing the Cp supporting ligand ($Cp = \eta^5\text{-}C_5H_5$) have been described.[7] When compared with Cp, the Tp ligand (Tp = hydridotris(pyrazolyl)borate) shows a pronounced tendency to stabilize η^2-acyl relative to η^1-acyl coordination,[8] and possible reasons for this difference have been thoroughly discussed.[8c]

Steric and electronic effects as well as metal oxophilicity[4] have been implicated as factors that influence the position

---

(1) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books; Mill Valley, CA, 1987. (b) Klingler, R. J.; Rathke, J. W. *Prog. Inorg. Chem.* **1991**, *39*, 113. (c) Kuhlmann, E. J.; Alexander, J. J. *Coord. Chem. Rev.* **1980**, *33*, 195.

(2) For some recent references with extensive bibliographies, see: (a) Bent, T. L.; Cotton, J. D. *Organometallics* **1991**, *10*, 3156. (b) Prock, A.; Giering, W. P.; Greene, J. E.; Meirowitz, R. E.; Hoffman, S. L.; Woska, D. C.; Wilson, M.; Chang, R.; Chen, J.; Magnuson, R. H.; Eriks, K. *Organometallics* **1991**, *10*, 3479. (c) Monti, D.; Bassetti, M.; Sunley, G. J.; Ellis, P.; Maitlis, P. *Organometallics* **1991**, *10*, 4015.

(3) (a) Mawby, R. J.; Basolo, F.; Pearson, R. G. *J. Am. Chem. Soc.* **1964**, *86*, 3994. (b) Wax, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 7028. (c) Martin, B. D.; Warner, K. E.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 33. (d) Webb, S. L.; Giandomenico, C. M.; Halpern, J. *J. Am. Chem. Soc.* **1986**, *108*, 345.

(4) For a recent review, see: Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059.

(5) (a) Carmona, E.; Sánchez, L.; Marín, J. M.; Poveda, M. L.; Atwood, J. L.; Priester, R. D.; Rogers, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 3214. (b) Carmona, E.; Contreras, L.; Poveda, M. L.; Sánchez, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 4322.

(6) (a) Carmona, E.; Wilkinson, G.; Rogers, R. D.; Hunter, W. E.; Zaworotko, M. J.; Atwood, J. L. *J. Chem. Soc., Dalton Trans.* **1980**, 229. (b) Carmona, E.; Marín, J. M.; Poveda, M. L.; Sánchez, L.; Rogers, R. D.; Atwood, J. L. *J. Chem. Soc., Dalton Trans.* **1983**, 1003. (c) Carmona, E.; Muñoz, M. A.; Rogers, R. D. *Inorg. Chem.* **1988**, *27*, 1598. (d) Carmona, E.; Sánchez, L. *Polyhedron* **1988**, *7*, 163. (e) Carmona, E.; Contreras, L.; Gutiérrez-Puebla, E.; Monge, A.; Sánchez, L. *Inorg. Chem.* **1990**, *29*, 700. (f) Carmona, E.; Contreras, L.; Poveda, M. L.; Sánchez, L. J.; Atwood, J. L.; Rogers, R. D. *Organometallics* **1991**, *10*, 61. (g) Carmona, E.; Contreras, L.; Gutiérrez-Puebla, E.; Monge, A.; Sánchez, L. J. *Organometallics* **1991**, *10*, 71.

(7) (a) Alt, H. G. *J. Organomet. Chem.* **1977**, *127*, 349. (b) Kreissl, F. R.; Sieber, W. J.; Keller, H.; Riede, J.; Wolfgruber, M. *J. Organomet. Chem.* **1987**, *320*, 83. (c) Kreissl, F. R.; Sieber, W. J.; Wolfgruber, M.; Riede, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 640. (d) Bonnesen, P. V.; Yau, P. K. L.; Hersh, W. H. *Organometallics* **1987**, *6*, 1587.

(8) (a) Desmond, T.; Lalor, F. J.; Ferguson, G.; Ruhl, B.; Parvez, M. *J. Chem. Soc., Chem. Commun.* **1983**, 55. (b) Curtis, M. D.; Shiu, K.-M.; Butler, W. M. *Organometallics* **1983**, *2*, 1475. (c) Curtis, M. D.; Shiu, K.-M.; Butler, W. M. *J. Am. Chem. Soc.* **1986**, *108*, 1550. (d) Rusik, C. A.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 4652. (e) Rusik, C. A.; Collins, M. A.; Gamble, A. S.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 2550.

(9) (a) Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1977**, *142*, C1. (b) Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1979**, *182*, C46. (c) Birk, R.; Berke, H.; Huttner, G.; Zsolnai, L. *J. Organomet. Chem.* **1986**, *309*, C18. (d) Bohle, D. S.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Shepard, W. E. B.; Wright, L. J. *J. Chem. Soc., Chem. Commun.* **1987**, 563. (e) Cardaci, G.; Bellachioma, G.; Zanazzi, P. *Organometallics* **1988**, *7*, 172. (f) Hermes, A. R.; Girolami, G. S. *Organometallics* **1988**, *7*, 394. (g) Bohle, D. S.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1988**, *358*, 411. (h) Birk, R.; Berke, H.; Huttner, G.; Zsolnai, L. *Chem. Ber.* **1988**, *121*, 1557. (i) Jablonski, C.; Bellachioma, G.; Cardaci, G.; Reichenbach, G. *J. Am. Chem. Soc.* **1990**, *112*, 1632.

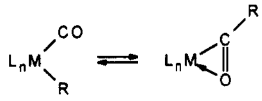
0276-7333/92/2311-3293$03.00/0

Table I. Electrochemical Data for Oxidation of 1a–1d

compd	E_{ox},[a] V vs Fc	$\Delta E_{p/2}$,[b] mV	n_{ox}[c]
$CpW(CO)_3Me$ (**1a**)	0.55[d]	75	2.1 (0.1)[d]
$CpW(CO)_3Et$ (**1b**)	0.52	89	1.9 (0.1)
$Cp'W(CO)_3Me$ (**1c**)	0.49	73	2.2 (0.1)
$CpW(CO)_2(PPh_3)Me$ (**1d**)	0.28	78	2.0 (0.1)

[a] Measured by derivative cyclic voltammetry (DCV).[11] Acetonitrile/0.1 M $Bu_4N^+PF_6^-$, Pt-disk microelectrode (d = 0.4 mm), voltage sweep rate ν = 1.0 V/s, 20 °C. [b] Derivative peak current width at half-height. [c] Faraday/mol required for complete oxidation of substrate, measured by constant-current coulometry. Average of three measurements with standard deviation in parentheses. [d] From ref 10.

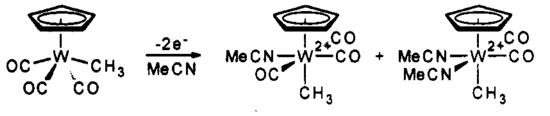
of an equilibrium between alkyl carbonyl and η^2-acyl complexes (eq 1). Steric congestion at the metal center,



(1)

caused by bulky alkyl groups R or sterically demanding auxiliary ligands, has been commonly considered to favor η^2-acyl formation.[6d,f,g,9e,i] Electron-rich metal centers on the other hand have been proposed to favor the alkyl carbonyl side of the equilibrium[6d,f,g] by virtue of the excellent π-acceptor properties of the CO ligand.

As part of our fascination with the electron-transfer chemistry of organotransition-metal complexes, we recently reported[10] that $CpW(CO)_3Me$ (**1a**) undergoes a 2-electron oxidation in acetonitrile to provide (eq 2) mixtures of the



(2)

1a **2a** **3a**

tungsten(IV) dications $CpW(CO)_3(NCMe)Me^{2+}$ (**2a**) and $CpW(CO)_2(NCMe)_2Me^{2+}$ (**3a**) as a result of 17/19-electron sequences in which the 19-electron cation radical $CpW(CO)_3(NCMe)Me^{\bullet+}$ was assumed to be a key intermediate. Fine-tuning of the reaction conditions facilitated the exclusive, high-yield formation of **3a** and made possible a further exploration of this and related compounds. Steric repulsions between the ligands within the presumed pseudooctahedral coordination sphere of these alkyl carbonyl dications must be quite severe. The high oxidation state should enhance the metal oxophilicity, and both factors may play a significant role in determining the reactivity of these complexes. Herein, we describe ligand substitution and CO insertion reactions of $CpW(CO)_2(NCMe)_2Me^{2+}$ and closely related tungsten(IV) dications.

Results and Discussion

Electrochemical Oxidation of Tungsten Alkyls. The chemical oxidations of $CpW(CO)_3Me$ (**1a**), $CpW(CO)_3Et$ (**1b**), $Cp'W(CO)_3Me$ (**1c**, Cp′ = η^5-C_5H_4Me), and $CpW(CO)_2(PPh_3)Me$ (**1d**) serve as the entry point to the key compounds in this study. Derivative cyclic voltammetry (DCV)[11] measurements show that these alkyls undergo chemically irreversible oxidations in the range 0.28–0.55 V vs the ferrocene/ferrocenium (Fc) couple (Table I) at voltage sweep rates up to 100 V/s. The electrode reactions exhibited near-Nernstian or quasi-reversible behavior, with derivative peak current width at half-height, $\Delta E_{p/2}$, ranging from 73 to 89 mV (cf. 70.3 mV for a Nernstian, chemically reversible 1-electron process;[12] we observe $\Delta E_{p/2}$ = 70–72 mV for the oxidation of ferrocene under the actual experimental conditions). Constant-current coulometry measurements in all cases indicated overall 2-electron oxidations.

Chemical Oxidation of Tungsten Methyl Complexes 1a, 1c, and 1d. As reported previously,[10] the chemical oxidation of **1a** with acetylferrocenium tetrafluoroborate, $Cp(\eta^5$-$C_5H_4COMe)Fe^+BF_4^-$ (E_{red} = 0.248 V vs Fc[13]) provided $CpW(CO)_3(NCMe)Me^{2+}$ (**2a**) and $CpW(CO)_2(NCMe)_2Me^{2+}$ (**3a**), the relative amounts of which could be manipulated by fine-tuning the reaction conditions. Attempts at obtaining X-ray diffraction quality crystals of **3a** with various counterions have been unsuccessful. It was hoped that the ring-methylated analogue $Cp'W(CO)_2(NCMe)_2Me^{2+}$ (**3c**) would prove more suitable for the task. This new compound was readily prepared following a procedure analogous to that employed for the synthesis of **3a** from **1a**, by the slow addition of an acetonitrile solution of 2 equiv of acetylferrocenium tetrafluoroborate to a vigorously stirred, dilute solution of **1c**. The product **3c**$(BF_4)_2$ was characterized by its IR, ^1H, and $^{13}C\{^1H\}$ NMR spectroscopic data as well as by elemental analysis (see the Experimental Section for details). Unfortunately, attempts at obtaining high-quality crystals also failed in this case.

No reaction other than the normal (vide infra) CO insertion reaction was observed when substitution of PPh_3 for the CO or acetonitrile ligands in **3a** was attempted. An alternative method for the preparation of phosphine-substituted derivatives of **3a** was sought in performing the oxidation of $CpW(CO)_2(PPh_3)Me$ (**1d**). However, treatment of **1d** with 2 equiv of $Cp_2Fe^+PF_6^-$ proceeded smoothly to give **3a** as the only W-containing product. This indicates that the presumed acetonitrile coordination at the incipient cation radical leads to preferential loss of PPh_3. Steric effects apparently exert a major influence on this reaction. With reference to the 17/19-electron transformations[14] that were suggested to be involved in the dication formation,[10] it may be reasonably argued that severe steric repulsive forces are relieved by PPh_3 dissociation from 19-electron $CpW(CO)_2(PPh_3)(NCMe)Me^{\bullet+}$. As a result, the reaction leads to 17-electron $CpW(CO)_2(NCMe)Me^{\bullet+}$, which was considered to be a key intermediate in the production of **3a** from **1a**.

Chemical Oxidation of $CpW(CO)_3Et$ (1b). Oxidation of **1b** with 2 equiv of acetylferrocenium tetrafluoroborate proceeded smoothly under the conditions employed for the synthesis of **3a** from **1a**, but to our initial surprise did not lead to the isolation of the anticipated dicationic species $CpW(CO)_2(NCMe)_2Et^{2+}$ (**3b**). Instead, the η^2-acyl complex $CpW(CO)(NCMe)_2(\eta^2$-$COEt)^{2+}$ (**4b**) was isolated in 73% yield as the bis(tetrafluoroborate) salt. The ^1H NMR spectrum of **4b** exhibited a Cp singlet at δ 6.19, a methyl triplet at δ 1.41, and two acetonitrile singlets at δ 2.40 and

---

(10) Skagestad, V.; Tilset, M. *Organometallics* **1991**, *10*, 2110.

(11) (a) Ahlberg, E.; Parker, V. D. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *121*, 73. (b) Parker, V. D. *Electroanal. Chem.* **1986**, *14*, 1.

(12) Ryan, O. B.; Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 2618.

(13) Britton, W. E.; Kashyap, R.; El-Hashash, M.; El-Kady, M.; Herberhold, M. *Organometallics* **1986**, *5*, 1029.

(14) For some recent reviews covering the chemistry of 17- and 19-electron species, see: (a) Astruc, D. *Chem. Rev.* **1988**, *88*, 1189. (b) Baird, M. C. *Chem. Rev.* **1988**, *88*, 1217. (c) Chanon, M., Julliard, M., Poite, J. C., Eds. *Paramagnetic Organometallic Species in Activation/Selectivity, Catalysis*; Kluwer Academic: Dordrecht, The Netherlands, 1989. (d) Trogler, W. C., Ed. *Organometallic Radical Processes*; Elsevier: Amsterdam, 1990. (e) Tyler, D. R.; Mao, F. *Coord. Chem. Rev.* **1990**, *97*, 119. (f) Astruc, D. *Acc. Chem. Res.* **1991**, *24*, 36. (g) Tyler, D. R. *Acc. Chem. Res.* **1991**, *24*, 325.

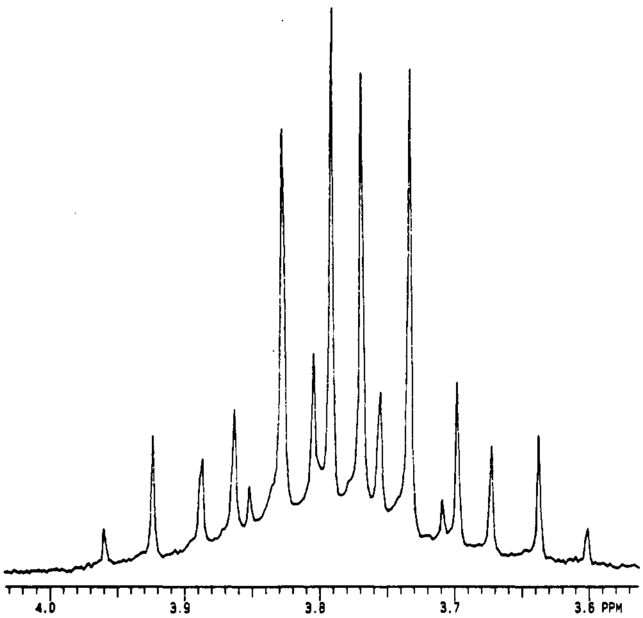
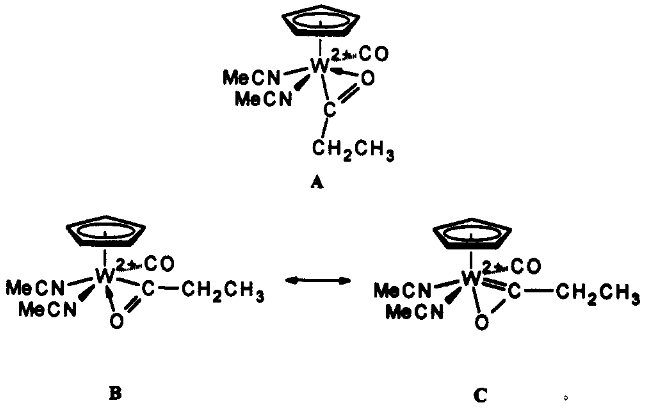


Figure 1. 200-MHz ^{1}H NMR spectrum showing the methylene resonances in the complex $CpW(CO)(NCMe)_2(\eta^2\text{-}COEt)^{2+}$ in acetonitrile-d_3.

2.72. The signals due to the methylene protons appeared as two overlapping doublets of quartets made up from the AB part of an ABX_3 pattern. The 16-line pattern of the AB part was located at δ 3.60–3.96 and is shown in Figure 1. The observation of only *one* Cp singlet and *one* methyl triplet strongly suggests that the complicated appearance of the methylene group signals is due to *diastereotopic* methylene hydrogens, rather than to the presence of more than one isomer of **4b** in solution. The presence of a terminal CO group was inferred from the IR spectrum which showed a band at 2082 cm^{-1}. The η^2-acyl CO could not be detected by IR spectroscopy. It is, however, not unreasonable that an η^2-acyl ligand may pass undetected by IR spectroscopy. For example, $TpMo(CO)_2(\eta^2\text{-}COMe)$ reportedly displayed a *weak* CO absorption at 1513 cm^{-1} in the infrared,[8c] and in some other cases the η^2-acyl CO absorptions have not been observed or identified.[7b,8e] The two CO groups in **4b** were discernible in the $^{13}C\{^1H\}$ NMR spectrum at δ 193.6 (CO) and 277.6 (*C*OEt). The resonance at δ 277.6 is particularly diagnostic and suggests the presence of an η^2-coordinated acyl group. The CO chemical shifts for such ligands commonly appear in the region 200–300 ppm.[4] The chemical shift values may be compared with those of a limited number of Mo(IV) and W(IV) η^2-acyl complexes with the general formula $CpMX_2(CO)(\eta^2\text{-}COR)$, which show ^{13}C NMR resonances at δ 276–279 for the acyl carbonyl and at δ 198–202 for the terminal CO.[7b,c]

The lack of symmetry indicated by the spectroscopic data for **4b**, viz. two acetonitrile ^{1}H NMR signals and the diastereotopic methylene hydrogens, are in accord with a structure in which the two acetonitrile ligands are positioned in a mutual cis relationship. If the complex is viewed as being derived from a "four-legged piano stool" structure with the η^2-acyl ligand occupying one coordination site, two structures A and B (Scheme I) that differ in the orientation of the C–O bond vector may be envisioned. An X-ray crystallographic analysis of the structure of the closely related compound $CpWCl_2(CO)(\eta^2\text{-}COEt)$, obtained by the addition of 2 equiv of HCl to the ethylidyne complex $CpW(CO)_2(CMe)$,[7b,c] revealed a "four-legged piano stool" structure in which the η^2-acyl ligand occupied one coordination site and was oriented in such a way that

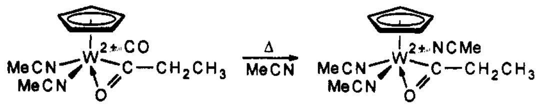
Scheme I. Possible Structures for 4b



the plane defined by W and the acyl CO was essentially perpendicular to the basal plane of the molecule. The acyl oxygen pointed away from the Cp ligand. In view of this, we favor structure B as the best description of **4b**. The possibility that an oxycarbene resonance form C contributes to the structure of the acyl ligand must also be considered, although the ^{13}C chemical shift suggests that the η^2-acyl description B is the dominant contributor.[4]

The oxidation of **1b** with acetylferrocenium tetrafluoroborate was performed at lower temperature in acetonitrile-d_3 in an attempt to detect the suspected intermediate dication $CpW(CO)_2(NCCD_3)_2Et^{2+}$ (**3b**-d_6) and observe its transformation into the η^2-acyl complex. At −40 °C, the ^{1}H NMR spectrum revealed the presence of **3b**-d_6 (δ 2.29 (t), 2.35 (q), 6.40 (s)) along with $CpW(CO)_3(NCCD_3)Et^{2+}$ (**2b**-d_3; δ 2.40 (m, 5 H), 6.54 (s, 5 H)) in a 1:3 ratio. The formation of the mixture of the two under the relatively high-concentration conditions of the experiment performed in the NMR tube was anticipated in view of the behavior of **1a** under similar conditions.[10] When the mixture was heated to ambient temperature, complete conversion of **3b**-d_6 to **4b**-d_6 was observed within minutes. Contrasting this behavior, **2b**-d_3 underwent no reaction at ambient temperature even during the course of several hours.

When solutions of **4b**$(BF_4)_2$ were heated in acetonitrile, a new species formed quantitatively by ^{1}H NMR spectroscopy (eq 3). The product was isolated in 63% yield and was identified as $CpW(NCMe)_3(\eta^2\text{-}COEt)^{2+}(BF_4^-)_2$



(3)

4b 5b

(**5b**$(BF_4)_2$). The terminal ν_{CO} absorption observed for **4b** in the infrared was now absent, but the $^{13}C\{^1H\}$ NMR spectrum still revealed the presence of an η^2-acyl group at δ 277.6. The ^{1}H NMR spectrum indicated two types of acetonitrile ligands (δ 2.44 (s, 6 H), 2.70 (s, 3 H)) and an ethyl group with equivalent methylene protons (δ 1.34 (t, 3 H), 3.70 (q, 2 H)). The Cp resonance was located at δ 5.83.

CO Insertion in $CpW(CO)_2(NCMe)_2Me^{2+}$ (3a). The solubility properties of **3a**$(BF_4)_2$ have precluded the investigation of its reactivity in solvents other than acetonitrile. The salt is insoluble in THF and dichloromethane and undergoes reactions in acetone and methanol to yield as yet unidentified products. During the course of several days at ambient temperature, acetonitrile-d_3 solutions of **3a**$(BF_4)_2$ underwent a quantitative (^{1}H NMR spectroscopy with internal standard) reaction to yield a new product.

Table II. Kinetic Data for the CO Insertion of 3a[a]

T, °C[b]	10^6k, s^{-1} [c]	T, °C[b]	10^6k, s^{-1} [c]
20.0	3.16 (0.12)	40.0	37.3 (2.2)
30.0	12.5 (0.39)	50.0	108 (6)

[a] In acetonitrile-d_3, monitored by ^{1}H NMR spectroscopy with hexamethylbenzene internal standard. [b] Stable to ±0.1 °C. [c] From linear regression of ln [**3a**] vs t data. One standard deviation in parentheses.

The ^{1}H NMR resonances due to the methyl and Cp ligands of **3a** at δ 1.49 and 6.40 were replaced by new singlets at δ 3.43 and 5.82, respectively. The coordinated acetonitrile signals vanished during the reaction, signaling ligand exchange with the solvent. When the reaction was performed in ordinary acetonitrile, followed by workup (see the Experimental Section for details), the product that was isolated in 74% yield displayed two coordinated acetonitrile singlets at δ 2.43 (6 H) and 2.69 (3 H). In view of the results obtained from the oxidation of CpW(CO)$_3$Et, we concluded that a combined CO insertion and ligand substitution reaction producing the η^2-acetyl complex CpW(NCMe)$_3$(η^2-COMe)$^{2+}$ (**5a**) had occurred. This assumption was corroborated by the ^{13}C{^{1}H} NMR spectrum which displayed a CO resonance at δ 276.1. In the infrared, no absorptions attributable to CO groups were observed. The isolated product gave a satisfactory elemental analysis for CpW(NCMe)$_3$(η^2-COMe)$^{2+}$(BF$_4^-$)$_2$. The methylcyclopentadienyl analogue Cp′W(NCMe)$_3$(η^2-COMe)$^{2+}$ (**5c**) was prepared from **3c** in a similar fashion.

The transformation of **3a** to **5a** formally involves a CO insertion into the tungsten–methyl bond accompanied by η^2-coordination of the resulting acetyl ligand, as well as a substitution of acetonitrile for the remaining CO ligand. A pertinent question in this regard is whether the substitution process precedes or succeeds the CO insertion reaction. On some occasions, samples of **3a** prepared from **1a** for reasons still unknown were contaminated with minor quantities (on the order of 5%) of a species whose ^{1}H NMR spectrum suggested the structure CpW(CO)(NCMe)$_2$(η^2-COMe)$^{2+}$ (**4a**; δ 6.22 (s, 5 H), 3.51 (s, 3 H)) by comparison with the spectrum of **4b**. Over time, the mixture of this compound and **3a** quantitatively yielded **5a** as the only observable product. The signals attributed to **4a** never increased in intensity during the course of this reaction and vanished at a rate somewhat greater than that of **3a**, and these observations at least suggest that CpW(CO)(NCMe)$_2$(η^2-COMe)$^{2+}$ is a competent intermediate for the formation of **5a** from **3a** and that CO substitution in fact succeeds CO insertion. Further support for this notion of course comes from the fact that CpW(CO)(NCMe)$_2$(η^2-COEt)$^{2+}$ undergoes the analogous transformation, as described already.

Kinetics of the CO Insertion Reaction of 3a. Because **4a** was never observed to build up during the conversion of **3a** to **5a** and in the cases when **4a** was present at the onset of the reaction was found to undergo reaction *faster* than **3a**, we feel confident that the observed rate of conversion of **3a** to **5a** actually reflects a rate-limiting CO insertion. Although interconversions and equilibria between alkyl carbonyl and η^2-acyl compounds have been frequently encountered, thermodynamic or kinetic data on the energetics of such reactions are remarkably scarce. This fact prompted us to investigate the reaction in detail. The kinetics of the CO insertion could be conveniently monitored by ^{1}H NMR spectroscopy in the temperature range 20–50 °C. Hexamethylbenzene (HMB) was used as an internal standard and showed that the reaction was quantitative (>95%) within the experimental detection limits. The intensity of the substrate Cp resonance was measured vs the HMB internal standard for 2.5–3.5 half-lives. At all temperatures, plots of ln [**3a**] vs t yielded straight lines, indicative of a first-order reaction in terms of **3a**. Table II displays kinetic data obtained at 20, 30, 40, and 50 °C. Figure 2 shows an Eyring plot of ln (k/T) vs 1000/T (K). Linear regression yields $\Delta H^\ddagger = 89.5 \pm 2.5$ kJ/mol, $\Delta S^\ddagger = -43.9 \pm 8.4$ J/(K·mol) (uncertainty given as one standard deviation), and by interpolation k(20 °C) $= 3.3 \times 10^{-6}$ s^{-1}. The somewhat negative $\Delta S^\ddagger$ appears to be in agreement with a unimolecular reaction with a relatively ordered transition state. For comparison, $\Delta S^\ddagger = -28 \pm 15$ J/(K·mol) was reported for the reversible (PPh$_2$Me)$_2$Fe(CO)$_2$(Me)(I) $\leftrightarrow$ (PPh$_2$Me)$_2$Fe(CO)(η^2-COMe)(I) interconversion which showed a significantly lower $\Delta H^\ddagger$ (41.9 ± 4 kJ/mol).[9i] The kinetic data for the latter reaction were obtained by line-shape analysis of exchange-broadened ^{13}C NMR spectra.

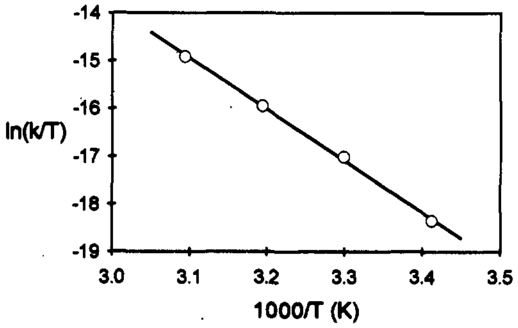


Figure 2. Eyring plot of the kinetic data for the CO insertion of CpW(CO)$_2$(NCMe)$_2$Me^{2+} (**3a**) in acetonitrile-d_3.

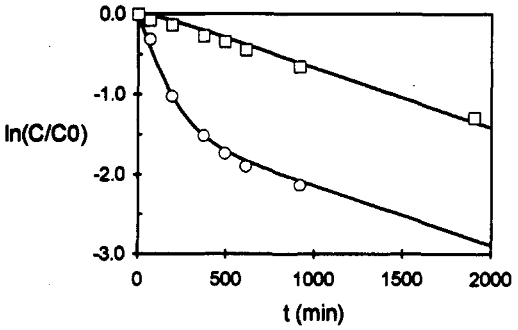
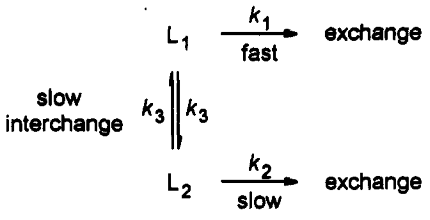


Figure 3. Plot of ln (fraction unexchanged) vs t for the exchange of the unique (circles) and the two identical (squares) acetonitrile ligands in **5a** for acetonitrile-d_3 at 20 °C, as monitored by ^{1}H NMR spectroscopy. The solid lines represent curves fitted according to Scheme II and eqs 4 and 5, as described in the text.

Acetonitrile Ligand Exchange in 5a. When solutions of **5a** and **5c** were left in acetonitrile-d_3 for prolonged time periods, it was noted that the intensities of the signals due to the coordinated acetonitrile ligands decreased, while a singlet at δ 1.95 arising from noncoordinated acetonitrile was superimposed on the residual solvent proton resonance multiplet centered at δ 1.93. This observation suggested ligand exchange with the solvent. For both complexes, it was noted that the unique acetonitrile ligand (located trans with respect to the η^2-acyl group) underwent exchange significantly faster than the two identical ligands (located cis relative to the η^2-acyl).

The kinetics of the acetonitrile exchange reactions of **5a** were monitored by ^{1}H NMR spectroscopy at 20 °C. Figure 3 displays the results from one kinetic run. Experimental data for the exchange reactions (circles for the fast exchange, squares for the slow exchange) are plotted as ln (fraction unexchanged) vs t in anticipation of first-order kinetics. First-order behavior is normally expected for simple exchange reactions, regardless of mechanism.[15a]

Scheme II



The curvature seen in Figure 3 suggests that a more complicated process is operative, in which the two exchange reactions are not independent of each other.

The curvature observed in Figure 3 and in all other runs involving the slow exchange of the unique acetonitrile ligand may be explained in terms of a slow intramolecular process that exchanges the different acetonitriles, coupled with first-order fast-exchange and slow-exchange reactions. This is shown schematically in Scheme II. L_1 here symbolizes the unique acetonitrile ligand, while L_2 indicates the two identical ones.

The rate constants k_1, k_2, and k_3 were evaluated by numerically fitting the experimental data according to this scheme, using eqs 4 and 5 to describe the exchange processes. The fractional terms are introduced because,

$$\frac{d[L_1]}{dt} = -k_1[L_1] - k_3[L_1] + \tfrac{1}{2}k_3[L_2] \qquad (4)$$

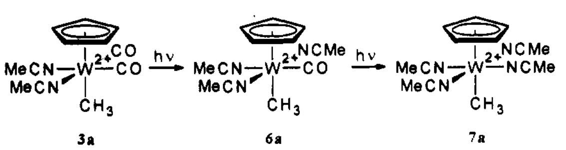
$$\frac{d[L_2]}{dt} = -\tfrac{1}{2}k_2[L_2] - \tfrac{1}{2}k_3[L_2] + k_3[L_1] \qquad (5)$$

presumably, only one acetonitrile in the L_2 couple may undergo exchange with the solvent (k_2) or undergo intramolecular interchange (k_3) at a time. The system was analyzed by a simple numerical integration technique in which each concentration derivative dC/dt was approximated as $\Delta C/\Delta t$, with the time increment Δt sufficiently small to make errors negligible.[15b] Values for Δt were chosen so that the conversion of L_1—the fastest process—was less than 5% per time step (the results were not significantly different with 2% conversion per step). For a given value of k_1, the values for k_2 and k_3 were adjusted by a trial-and-error procedure until the best possible fit of experimental and calculated concentration vs time profiles was obtained (judged by visual inspection of experimental data and the simulated curve and by a least-squares procedure). The whole process may be conveniently performed on any commercially available spreadsheet program for desktop computers.

The best fit that was obtained for the particular run in Figure 3 is indicated by the solid lines and corresponds to $k_1 = 1.0 \times 10^{-4}\ s^{-1}$, $k_2 = 0.04 \times 10^{-4}\ s^{-1}$, and $k_3 = 0.26 \times 10^{-4}\ s^{-1}$. For different runs, k_1 was reproducible to ±15%, whereas k_2 showed even greater variation (in some cases, the best fits were obtained with $k_2 = 0$). The modeling showed that the slope of the initial part of the curve for the fast-exchange process (ca. 1–1.5 half-lives) was relatively insensitive to the magnitudes of k_2 and k_3 as long as k_1 was significantly greater than k_2 and k_3. Obviously, the slow interchange of L_1 and L_2 is only observable when L_1 has undergone significant exchange. In conclusion, the two ligand-exchange reactions *are* coupled to each other via the slow intramolecular interchange reaction (k_3). However, on the basis of repeated experiments it remains somewhat uncertain whether the slow exchange occurs exclusively as a consequence of the intramolecular interchange, of if the separate intermolecular exchange reaction (k_2) is also operative.

PPh_3-Catalyzed Acetonitrile Exchange in 5a. While quite unsuccessfully attempting to achieve ligand substitution reactions at **5a** with PPh_3, we accidentally noted that the presence of PPh_3 caused a great acceleration of the rate of exchange of the two equivalent acetonitrile ligands with solvent acetonitrile-d_3, whereas the rate of exchange of the unique acetonitrile ligand appeared not to be affected. No intermediates were observed for this PPh_3-catalyzed ligand-exchange process. In the presence of 0.2 and 0.4 equiv of PPh_3 (40 mM substrate) at 17 °C, pseudo-first-order kinetic behavior was observed with $k_{obs} = 5.5 \times 10^{-4}$ and $11.6 \times 10^{-4}\ s^{-1}$, respectively. The data indicate a first-order dependence of this exchange process on the PPh_3 concentration. Variable-temperature runs at 14–37 °C (8 mM PPh_3) gave $\Delta H^* = 51 \pm 5$ kJ/mol, $\Delta S^* = -91 \pm 15$ J/(K·mol), and $k(20\ °C) = 0.11\ M^{-1}\ s^{-1}$ by interpolation. The data correspond to a pseudo-first-order rate constant $k_{obs} = 9 \times 10^{-4}\ s^{-1}$ at 20 °C, or a rate enhancement at this particular PPh_3 concentration, compared with the uncatalyzed exchange of these ligands, of about 220! While the activation entropy hints at associative kinetics, the mechanism of the reaction remains obscure. Nucleophilic attack at the acetyl methyl group, with the formation of $(CH_3)PPh_3^+$ and $CpW(CO)(NCMe)_3^+$ as hypothetical intermediates, has been ruled out by a crossover experiment. The addition of $(CD_3)PPh_3^+I^-$ to the reaction mixture failed to generate detectable quantities of $(CH_3)PPh_3^+$. Attack by PPh_3 at the acetyl or cyclopentadienyl ligands could generate dicationic intermediates with one formal positive charge at the phosphorus and one at the metal center. The attenuated charge at the metal could cause a labilization of the donor ligands, but this suggestion fails to explain the selective labilization of the two identical ligands. Concerning the influence of the metal charge, it is noteworthy that the acetonitrile ligand in *cis*-$CpW(CO)_2(NCMe)Me$ (prepared in situ by reduction of **3a** with 2 equiv of cobaltocene[10]) is substitutionally labile and undergoes facile substitution in the presence of PPh_3 in acetonitrile-d_3. The reaction initially yields *cis*-$CpW(CO)_2(PPh_3)Me$ which undergoes slow isomerization to the thermodynamically more stable trans isomer.

Photochemical CO Substitution in $CpW(CO)_2(NCMe)_2Me^{2+}$ (3a). Although the attempts to effect thermal CO substitution in **3a** with PPh_3 were unsuccessful, efforts were made at initiating a photochemical substitution. Low-pressure mercury lamp irradiation through Pyrex glass of a solution of $\mathbf{3a}(BF_4)_2$ in acetonitrile in the presence of PPh_3 for 30 min at 0 °C (in order to minimize thermal CO insertion) caused the disappearance of **3a** and formation of a mixture of two new products (eq 6), assigned the structures $CpW(CO)(NCMe)_3Me^{2+}$ (**6a**; ^1H NMR δ 1.48 (s, 3 H), 2.58 (s, 6 H), 2.60 (s, 3 H), 6.05 (s, 5 H); IR ν_{CO} 2020 cm^{-1}) and $CpW(NCMe)_4Me^{2+}$ (**7a**; ^1H NMR δ 1.38 (s, 3 H), 2.74 (s, 12 H), 5.48 (s, 5 H)). The ^1H NMR spectroscopic data for **7a** require that the methyl group must be located trans with respect to the Cp, thereby rendering the acetonitrile ligands identical. The geometry of **6a** is assumed to be similar, but the data are equally consistent with a structure in which the methyl and CO



3a **6a** **7a** (6)

---

[15] (a) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981. (b) Wiberg, K. In *Investigation of Rates and Mechanisms of Reactions*; Lewis, E. S. (Ed.); Techniques of Chemistry; Wiley-Interscience: New York, 1974; Vol. VI, Part 1, p. 764.

Table III. Comparison of ^{1}H NMR and Electrochemical Data for Complexes $CpW(CO)_{4-n}(NCMe)_nMe^{2+}$ (n = 1–4)

compd	^{1}H NMR^a δ (MeCN)	δ (Cp)	δ (Me)	E_{red},^{b} V vs Fc
$CpW(CO)_3(NCMe)Me^{2+}$ (**2a**)	2.58	6.60	1.53	−0.80^c
$CpW(CO)_2(NCMe)_2Me^{2+}$ (**3a**)	2.58	6.40	1.49	−1.00
$CpW(CO)(NCMe)_3Me^{2+}$ (**6a**)	2.58 (6 H), 2.60 (3 H)	6.05	1.48	−1.29^d
$CpW(NCMe)_4Me^{2+}$ (**7a**)	2.74	5.48	1.38	−1.57

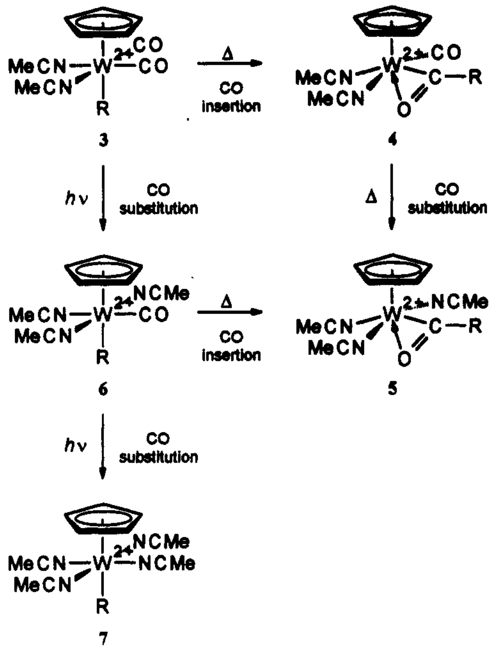
^{a} In acetonitrile-d_3. ^{b} Cyclic voltammetry peak potentials for chemically irreversible reductions (1.0 mM substrate in acetonitrile/0.1 M $Bu_4N^+PF_6^-$, voltage sweep rate ν = 1.0 V/s, Pt-disk electrode (d = 0.4 mm), 20 °C. ^{c} Measurement done on a 3:1 mixture of **3a**$(BF_4)_2$ and **2a**$(BF_4)_2$. ^{d} Measurement done on a 1:1 mixture of **6a**$(BF_4)_2$ and **7a**$(BF_4)_2$.

groups are interchanged. Prolonged irradiation caused an increase in the amount of **7a** at the expense of **6a**, suggesting that **6a** is an intermediate in the generation of **7a**. **7a**$(BF_4)_2$ was isolated in 67% yield. A broad, low-intensity disruption of the base line of the ^{1}H NMR spectrum in the region δ 7.4–8.0 indicated that the sample was slightly contaminated with small amounts of a material of unknown composition. Repeated crystallizations of **7a**$(BF_4)_2$ failed to remove this impurity. In order to eliminate the possibility that this broad signal belonged to the product, a photolysis was carried out in the absence of PPh_3, but otherwise under identical conditions. Now, the isolated product mixture contained **7a** and **5a** in an approximate 1:1 ratio. Under these conditions, it appears that the thermal conversion of **3a** to **5a** competed with the photochemical reaction leading to **7a** due a less efficient photochemical reaction. An independent photolysis of **5a** led to no reaction, eliminating the possibility that **5a** is an intermediate for the formation of **7a**. The presence of PPh_3 appears to catalyze the photosubstitution of acetonitrile for CO in **3a** by some unknown mechanism.

When a mixture of **6a** and **7a** was heated in acetonitrile, **6a** quantitatively underwent CO insertion to produce the η^2-acetyl complex **5a**, whereas **7a** underwent no reaction. No evidence for thermal CO substitution at **6a** to produce **7a** was observed.

Comparison of Spectroscopic and Electrochemical Properties of $CpW(CO)_{4-n}(NCMe)_nMe^{2+}$ (n = 1–4). Herein and in our previous paper,[10] we have described the observation and/or isolation of the series of dicationic methyltungsten complexes $CpW(CO)_{4-n}(NCMe)_nMe^{2+}$ (n = 1–4) in which the electron density at the metal progressively increases throughout the series due to the introduction of donor acetonitrile ligands.[16] A gradual change in the electronic properties is clearly discerned by comparison of the ^{1}H NMR (Cp and Me) chemical shifts and the electrochemical reduction potentials for the dications. The data are summarized in Table III. The reduction potentials for the dications are particularly diagnostic. Although all potentials refer to chemically irreversible processes (at voltage sweep rates at least as high as 100 V/s) and quantitative comparisons of the potentials for thermodynamic purposes should be done with caution, the data show that the replacement of one carbonyl ligand by acetonitrile causes the reduction potential E_{red} to shift in the cathodic direction by 0.26 V on the average, and a near additive effect of the ligand substitution on E_{red} is observed. The changes are greatest for the last two substitutions. This effect may be attributed to that fact that for each acetonitrile ligand that is introduced, the number of remaining carbonyls left to accommodate the increased electron density has been reduced. In spite of this trend, the reduction peak potentials correlate well (r = 0.997) with Lever's additive ligand parameters E_L.[17] Using E_L = 0.99 for the carbonyl and 0.34 for the acetonitrile ligands, the Lever correlation yields a straight line, $E_{red} = 0.40(\sum E_L) - 2.10$. The intercept −2.10 includes E_L parameters, not available in Lever's tabulations, for the Cp and methyl ligands, along with terms depending on the nature of the metal and its oxidation state as well as the choice of reference electrode. The slope of 0.40 according to Lever's interpretation should reflect a rather poor ligand binding in the W(III) cation radical relative to in the W(IV) dication state. As a reference, Ru(III)/Ru(II) couples per definition exhibit a slope of 1.0 in similar correlations. The inferred instability of the W(III) state is corroborated by the observed chemically irreversible voltammetric behavior and is further reflected in the not too surprising finding that the cobaltocene reductions of **3a** and **2a** lead to loss of donor acetonitrile ligands.[10]

Scheme III



Concluding Remarks

In this paper, we have presented results that describe the interrelation between a number of novel isolated and/or observed tungsten(IV) alkyl and acyl dications. The reactions that interconnect these complexes are summarized in Scheme III. For R = Me, all transformations have been observed; for R = Et, only the interconversions between **3** and **4**, and between **4** and **5**, have been attempted and observed.

The rate of CO insertion in **3** to give **4** reveals a most striking difference in the behavior of the methyl and the ethyl series. Whereas **3a** underwent smooth transformation to **4a** only after several days at ambient temperature, **3b** provided **4b** within minutes. Electronically, the differences between **3a** and **3b** should be only modest, as indirectly indicated by the near equal oxidation potentials measured for **1a** and **1b**. The difference in reactivity is therefore most likely attributable to steric effects. The coordination sphere at pseudo-octahedral **3a** is rather crowded and the strain is alleviated by conversion to **4a**. The repulsive forces in **3b** are more severe and cause the

---

(16) For a review of the coordination chemistry of nitriles, see: Storhoff, B. N.; Lewis, H. C., Jr. *Coord. Chem. Rev.* **1977**, *23*, 1.

(17) Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271.

transformation to **4b** to proceed even faster.

Another striking observation is that **3a** readily transforms into **4a**, whereas the analogous CO insertions of **2a** and **2b** to give corresponding η^2-acyl complexes CpW(CO)$_2$(NCMe)(η^2-COR)$^{2+}$ (R = Me, Et) are not observed. This observation is not readily reconciled with steric effects since near the metal center, the spatial demands of the acetonitrile ligand should not be dramatically different from that of a carbonyl group. On the other hand, if the rate difference is due to electronic effects, these reactions are in contrast with earlier observations which led to the suggestion that donor ligands should favor the alkyl carbonyl relative to the η^2-acyl isomeric form.[6d,f,g] It is not presently clear whether the different reactivity is due to a purely kinetic effect or if the failure to form CpW(CO)$_2$(NCMe)(η^2-COR)$^{2+}$ also reflects a thermodynamic preference for the alkyl carbonyl form. In any event, the results suggest that it may not be universally true that donor ligands favor the alkyl carbonyl form. More data are clearly needed in order to assess the influence of electronic effects as a function of the nature of the metal, its oxidation state, ancillary ligands, and exact coordination geometry.

Experimental Section

General Procedures. Organometallic complexes were handled under inert atmosphere by use of standard vacuum line, Schlenk, syringe, and drybox techniques. Acetonitrile was distilled from P_2O_5, and acetonitrile-d_3 was distilled from CaH_2. ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were recorded on Varian Gemini-200 and Varian XL-300 instruments. Chemical shifts are reported downfield from tetramethylsilane using the residual solvent proton resonances as internal standards (δ 1.93 (^{1}H NMR) and δ 1.3 (^{13}C{^{1}H} NMR) for acetonitrile). IR spectra were obtained on a Perkin-Elmer 1310 infrared spectrophotometer. Melting points were measured on a Büchi melting point apparatus in capillary tubes sealed under vacuum. Elemental analyses were performed by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, Germany.

The electrochemical measurements were performed with an EG&G-PAR Model 273 potentiostat driven by a HP 3314A function generator. Positive feedback compensation for uncompensated resistance was employed. The electrochemical cells, data-handling procedures, and electrodes have been previously described.[11a,18] The Ag/AgNO$_3$ reference electrode was calibrated against separate solutions of ferrocene. Electrolytes that were employed for electrochemical experiments were passed through a column of active neutral alumina before use in order to remove water and protic impurities. The electrolyte was freed of air by purging with purified argon, and all electrochemical experiments were carried out under a blanket of solvent-saturated argon gas. Constant-current coulometry experiments in which the substrate disappearance was monitored by DCV were performed at a Pt-gauze working electrode in a H-shaped cell, the compartments of which were separated by a fritted-glass junction.

The constant-temperature water bath employed for kinetics was a Heto CB 10 cooling bath equipped with a Hetotherm DT thermostat that ensured a better than ±0.1 °C temperature stability.

Compounds CpW(CO)$_3$Me,[19a] CpW(CO)$_3$Et,[19a] CpW(CO)$_2$(NCMe)$_2$Me^{2+}(BF$_4^-$)$_2$,[10] Cp$_2$Fe$^+$BF$_4^-$,[19b] and acetylferrocenium tetrafluoroborate[19c] were prepared according to published procedures.

Cp′W(CO)$_3$Me (1c). An acetonitrile (50-mL) solution of W(CO)$_6$ (1000 mg, 2.84 mmol) was heated at reflux for 72 h to generate W(CO)$_3$(NCMe)$_3$. The solvent was removed by vacuum transfer, and THF (40 mL) was added. Freshly cracked methylcyclopentadiene (0.53 mL, 4.2 mmol) was added, and the solution was heated at reflux for 3 h. The solution was cooled to −78 °C, and *n*-BuLi (2.2 mL of a 1.6 M hexane solution, 3.5 mmol) was added. The mixture was warmed to ambient temperature. Iodomethane (440 μL, 7.0 mmol) was added at −40 °C. The solvent was removed in vacuo at 0 °C. The oily residue was sublimed under vacuum to yield **1c** as yellow needles (680 mg, 65%) judged pure by ^{1}H NMR and IR spectroscopy: ^{1}H NMR (chloroform-*d*) δ 0.37 (s, 3 H), 2.05 (s, 3 H), 5.19 (m, 2 H), 5.27 (m, 2 H); IR (acetonitrile) ν_{CO} 2003, 1905 cm^{-1}.

CpW(CO)$_2$(PPh$_3$)Me (1d). This complex has been previously prepared by the photolysis of CpW(CO)$_3$Me in the presence of PPh$_3$.[19d] We utilized a different procedure for its preparation. A solution of CpW(CO)$_2$(PPh$_3$)H[19e] (550 mg, 0.94 mmol) in THF (30 mL) was cooled at −78 °C and treated with *n*-BuLi (1.0 mL of a 1.6 M hexane solution, 1.6 mmol). The solution was stirred for 1 h and then heated to −30 °C, which caused the precipitation of a yellow solid. Iodomethane (200 μL, 3.2 mmol) was added at −30 °C, and the mixture was heated to 0 °C and stirred until a homogeneous solution was obtained. The solvent was removed by vacuum transfer. The product was separated by column chromatography (SiO$_2$, hexane/toluene) and recrystallized from hexane/acetonitrile as yellow crystals (400 mg, 71%), with ^{1}H NMR and IR spectra matching those reported.[19d]

Cp′W(CO)$_2$(NCMe)$_2$Me^{2+}(BF$_4^-$)$_2$ (3c(BF$_4$)$_2$). A solution of acetylferrocenium tetrafluoroborate (136 mg, 0.44 mmol) in acetonitrile (3 mL) was slowly added to a solution of **1c** (80 mg, 0.22 mmol) in acetonitrile (50 mL) at 0 °C at such a rate that the blue ferrocenium color was never persistent. The product was precipitated by the addition of ether at −20 °C. The solvent was decanted, and the product was recrystallized from acetonitrile/ether to give yellow crystals (80 mg, 62%): mp 128–130 °C; ^{1}H NMR (acetonitrile-d_3) δ 1.52 (s, 3 H), 2.43 (s, 3 H), 2.61 (s, 6 H), 6.12 ("t", J = 2.4 Hz, 2 H), 6.21 ("t", J = 2.4 Hz, 2 H); ^{13}C{^{1}H} NMR (acetonitrile-d_3) δ 3.8, 15.1, 28.4, 86.4, 100.2, 135.2, 195.8; IR (acetonitrile) ν_{CO} 2102, 2060 cm^{-1}. Anal. Calcd for $C_{13}H_{16}B_2F_8N_2O_2W$: C, 26.48; H, 2.73; N, 4.75. Found: C, 26.19; H, 2.76; N, 5.28.

CpW(CO)(NCMe)$_2$(η^2-COEt)$^{2+}$(BF$_4^-$)$_2$ (4b(BF$_4$)$_2$). A solution of acetylferrocenium tetrafluoroborate (54 mg, 0.17 mmol) in acetonitrile (4 mL) was added dropwise to a vigorously stirred solution of CpW(CO)$_3$Et (30 mg, 0.083 mmol) in acetonitrile (20 mL) at ambient temperature at such a rate that the blue ferrocenium color never was persistent. The solution was concentrated to 5 mL, layered with ether, and stored at −20 °C. Yellow crystals formed within 24 h (38 mg, 73%): mp 85 °C dec; ^{1}H NMR (acetonitrile-d_3) δ 1.41 (t, J = 7.2 Hz, 3 H), 2.40 (s, 3 H), 2.72 (s, 3 H), 3.75 (dq, J = 19.1, 7.2 Hz, 1 H), 3.81 (dq, J = 19.1, 7.2 Hz, 1 H), 6.19 (s, 5 H); ^{13}C{^{1}H} NMR (acetonitrile-d_3) δ 4.7, 9.9, 39.4, 99.5, 193.6, 277.6; IR (acetonitrile) ν_{CO} 2082 cm^{-1}. Anal. Calcd for $C_{13}H_{16}B_2F_8N_2O_2W$: C, 26.48; H, 2.73; N, 4.75. Found: C, 26.30; H, 2.96; N, 5.32.

CpW(NCMe)$_3$(η^2-COMe)$^{2+}$(BF$_4^-$)$_2$ (5a(BF$_4$)$_2$). A solution of acetylferrocenium tetrafluoroborate (100 mg, 0.28 mmol) in acetonitrile (3 mL) was added dropwise to a vigorously stirred solution of CpW(CO)$_3$Me (180 mg, 0.52 mmol) in acetonitrile (20 mL) at 20 °C at such a rate that the blue ferrocenium color was never persistent. As described previously,[10] this procedure ensures that CpW(CO)$_3$(NCMe)Me^{2+} is not formed along with the desired CpW(CO)$_2$(NCMe)$_2$Me^{2+}. The solution containing CpW(CO)$_2$(NCMe)$_2$Me^{2+} was heated at reflux for 3 h during which the reaction was monitored by IR spectroscopy. The solution was cooled to ambient temperature, concentrated, and layered with ether. The product crystallized as orange microcrystals by cooling to −20 °C (122 mg, 74%): mp 178–180 °C; ^{1}H NMR (acetonitrile-d_3) δ 2.43 (s, 6 H), 2.69 (s, 3 H), 3.42 (s, 3 H), 5.82 (s, 5 H); ^{13}C{^{1}H} NMR (acetonitrile-d_3) δ 4.6, 30.4, 100.0, 132.5, 276.1. Anal. Calcd for $C_{13}H_{17}B_2F_8N_3OW$: C, 26.52; H, 2.91; N, 7.14. Found: C, 26.19; H, 2.89; N, 7.81.

CpW(NCMe)$_3$(η^2-COEt)$^{2+}$(BF$_4^-$)$_2$ (5b(BF$_4$)$_2$). The acetonitrile solution of crude **4b**(BF$_4$)$_2$, prepared as described above, was heated at reflux for 3 h. The solution was concentrated,

---

[18] (a) Ahlberg, E.; Parker, V. D. *Electroanal. Chem. Interfacial Electrochem.* **1981**, *121*, 57. (b) Ahlberg, E.; Parker, V. D. *Acta Chem. Scand., Ser. B* **1980**, *34B*, 97. (c) Tilset, M. In *Energetics of Organometallic Species*; Simões, J. A. M., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; p 109.

[19] (a) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 304. (b) Nesmeyanov, A. N.; Perevalova, E. G.; Yuryeva, L. P.; Grandberg, K. I. *Izv. Akad. Nauk SSSR* **1962**, 1772. (c) Carty, P.; Dove, M. F. A. *J. Organomet. Chem.* **1971**, *28*, 125. (d) Severson, R. G.; Wojcicki, A. *J. Organomet. Chem.* **1978**, *157*, 173. (e) Kalck, P.; Poilblanc, R. *C. R. Acad. Sci. Paris, Ser. C* **1968**, *267*, 536.

layered with ether, and cooled to −20 °C to give the product as red needles (31 mg, 63%); mp 202–208 °C dec; ^{1}H NMR (acetonitrile-d_3) δ 1.34 (t, *J* = 7.2 Hz, 3 H), 2.44 (s, 6 H), 2.70 (s, 3 H), 3.70 (q, *J* = 7.2 Hz, 2 H), 5.83 (s, 5 H); ^{13}C{^{1}H} NMR (acetonitrile-d_3) δ 4.5, 9.9, 37.8, 99.0, 131.9, 277.6. Anal. Calcd for $C_{14}H_{19}B_2F_8N_3OW$: C, 27.90; H, 3.18; N, 6.97. Found: C, 27.95; H, 3.17; N, 7.05.

$Cp'W(NCMe)_3(\eta^2\text{-}COMe)^{2+}(BF_4^-)_2$ (5c(BF$_4$)$_2$). A solution of acetylferrocenium tetrafluoroborate (170 mg, 0.54 mmol) in acetonitrile (3 mL) was added slowly to a solution of **1c** (100 mg, 0.27 mmol) in acetonitrile (50 mL). The solution was heated at reflux for 3 h, cooled to ambient temperature, and concentrated to 4 mL. The product formed as orange crystals by layering with ether at −20 °C (120 mg, 73%): mp 138–142 °C; ^{1}H NMR (acetonitrile-d_3) δ 2.31 (s, 3 H), 2.71 (s, 6 H), 3.37 (s, 3 H), 5.63 (br s, 4 H); ^{13}C{^{1}H} NMR (acetonitrile-d_3) δ 4.7, 14.5, 29.1, 92.7, 99.0, 130.0, 273.3. Anal. Calcd for $C_{14}H_{19}B_2F_8N_3OW$: C, 27.90; H, 3.17; N, 6.97. Found: C, 27.10; H, 3.31; N, 7.73.

$CpW(NCMe)_4Me^{2+}(BF_4^-)_2$ (7a(BF$_4$)$_2$). A solution of **3a**(BF$_4$)$_2$ (40 mg, 0.07 mmol) and PPh$_3$ (19 mg, 0.07 mmol) in acetonitrile (30 mL) was irradiated with a low-pressure Hg lamp through Pyrex glass for 16 h at 0 °C. The solution was concentrated to 10 mL, layered with ether, and cooled to −20 °C. The product formed as red crystals (28 mg, 67%): mp 92–96 °C; ^{1}H NMR (acetonitrile-d_3) δ 1.38 (s, 3 H), 2.74 (s, 12 H), 5.48 (s, 5 H); ^{13}C{^{1}H} NMR (acetonitrile-d_3) δ 4.1, 54.8, 99.4. Anal. Calcd for $C_{14}H_{20}B_2F_8N_4W$: C, 27.94; H, 3.35; N, 9.31. Found: C, 28.92; H, 3.98; N, 7.52. The ^{1}H NMR spectrum showed a faint, broad signal at δ 7.4–8.0, which could not be removed by repeated recrystallizations.

This experiment was repeated in the absence of PPh$_3$ but otherwise under identical conditions. This procedure led to the isolation of a 1:1 mixture of **7a**(BF$_4$)$_2$ and **5a**(BF$_4$)$_2$ (25 mg, 65%).

Oxidation of $CpW(CO)_3Et$ (1b) in Acetonitrile-d_3. An NMR tube equipped with a ground-glass joint was loaded with **1b** (10 mg, 0.027 mmol) and acetylferrocenium tetrafluoroborate (18 mg, 0.057 mmol). Acetonitrile-d_3 (0.5 mL) was added at liquid N$_2$ temperature by vacuum transfer, and the tube was sealed under vacuum. The tube was transferred to the NMR probe, precooled at −40 °C, and the ^{1}H NMR spectrum was recorded immediately. The spectrum revealed the presence of $CpW(CO)_2(NCCD_3)_2Et^{2+}$ (**3b**-d_6) (δ 2.29 (t), 2.35 (q), 6.40 (s)—partially overlapping peaks and less than optimum resolution precluded extraction of accurate coupling constants) and $CpW(CO)_3(NCCD_3)Et^{2+}$ (**2b**-d_3) (δ 2.40 (m, 5 H), 6.54 (s, 5 H)) in a 1:3 ratio. When the mixture was heated to ambient temperature, **3b**-d_6 underwent complete transformation to $CpW(CO)(NCCD_3)_2(\eta^2\text{-}COEt)^{2+}$ (**4b**-d_6) within minutes. On the other hand, for **2b**-d_3 there was no sign of reaction even after 10 h.

Oxidation of $CpW(CO)_2(PPh_3)Me$ (1d) with $Cp_2Fe^+BF_4^-$. Starting with **1d** (70 mg, 0.12 mmol) and $Cp_2Fe^+BF_4^-$ (63 mg, 0.024 mmol), the experiment was performed according to the procedure used for the preparation of **3a**(BF$_4$)$_2$ from **1a**.[10] The isolated yield of **3a**(BF$_4$)$_2$ was 72%.

Thermal Reaction of $CpW(CO)_3(NCMe)Me^{2+}$ and $CpW(CO)_2(NCMe)_2Me^{2+}$ in Acetonitrile-d_3. A 1:3 mixture of $CpW(CO)_3(NCCD_3)Me^{2+}$ (**2a**-d_3) and $CpW(CO)_2(NCCD_3)_2Me^{2+}$ (**3a**-d_6) was generated by the oxidation of **1a** with 2 equiv of acetylferrocenium tetrafluoroborate in acetonitrile-d_3 in a sealed NMR tube at 0 °C as described previously.[10] At ambient temperature, **3a**-d_6 slowly reacted to provide $CpW(NCCD_3)_3(\eta^2\text{-}COMe)^{2+}$ (**5a**-d_9) while no reaction took place for **2a**-d_3. The contents were heated at reflux for 4 h. A ^{1}H NMR spectrum revealed that **3a**-d_6 had undergone complete (the solvent residual proton resonances were used as a rough internal standard) transformation to **5a**-d_9, whereas **2a**-d_3 had undergone decomposition to unidentified materials giving rise to several singlets in the region δ 5.6–6.0 and very faint signals at δ 3.3–3.4. The dominant Cp-containing species were located at δ 6.02 (coinciding with $CpW(CO)_3(NCMe)^+$ [20]) and δ 5.94.

Kinetics of the CO Insertion Reaction of $CpW(CO)_2(NCMe)_2Me^{2+}$ (3a). An NMR tube equipped with a ground-glass joint was loaded with **3a**(BF$_4$)$_2$ (9.5 mg, 0.016 mmol) and hexamethylbenzene (HMB; ca. 1.0 mg, 0.006 mmol). Acetonitrile-d_3 (0.5 mL) was added by vacuum transfer, and the tube was sealed under vacuum. ^{1}H NMR spectra were recorded at suitable time intervals, and the intensity of the substrate Cp resonance was measured relative to that of HMB for ca. 3 half-lives or more. The coordinated acetonitrile resonances expected for the product **5a** were absent, indicating that exchange with the solvent took place during the reaction and the product therefore was $CpW(NCCD_3)_3(\eta^2\text{-}COMe)^{2+}$ (**5a**-d_9). The coordinated acetonitrile signal intensity for the substrate decreased more rapidly than the Cp signal intensity, showing that ligand exchange for the solvent was rapid in comparison to the CO insertion reaction. Between the recording of the NMR spectra, the tube was immersed in the constant-temperature water bath. The kinetic data are summarized in the Results and Discussion. The presence of the HMB internal standard established that the conversion to **5a** was quantitative within detection limits.

Kinetics of the Acetonitrile Ligand-Exchange Reactions of $CpW(NCMe)_3(\eta^2\text{-}COMe)^{2+}$ (5a). An NMR tube that was equipped with a ground-glass joint was loaded with **5a**(BF$_4$)$_2$ (10.8 mg, 0.018 mmol). Acetonitrile-d_3 (0.5 mL) was added by vacuum transfer, and the tube was sealed under vacuum. The progress of the exchange processes was followed by monitoring the decrease in the intensities of the signals due to the coordinated acetonitrile relative to the acetyl methyl group as an internal standard. The tube was immersed in the constant-temperature water bath at 20.0 °C between NMR runs. The kinetic data are described and summarized in the Results and Discussion. HMB internal standard was employed for some runs and verified that the ligand exchange took place without sample deterioration.

Kinetics of the PPh$_3$-Catalyzed Acetonitrile Ligand-Exchange Reactions of $CpW(NCMe)_3(\eta^2\text{-}COMe)^{2+}$ (5a). To an NMR tube that was equipped with a ground-glass joint was added 500 μL (corresponding to 0.0034 mmol of PPh$_3$) of an ether solution of PPh$_3$ (2.7 mg in 1.50 mL). To another tube was added 1.0 mL (0.0069 mmol) of the same PPh$_3$ solution. The ether was removed in vacuo. A freshly prepared solution of **5a**(BF$_4$)$_2$ (10 mg, 0.017 mmol) and HMB (1.0 mg, 0.006 mmol) in acetonitrile-d_3 (0.43 mL) was added to each tube. The tubes, now containing 40 mM solutions of **5a**(BF$_4$)$_2$ and 8 or 16 mM of PPh$_3$, respectively, were sealed under vacuum and kept at liquid N$_2$ temperature until the experiments were initiated. The tubes were inserted into the NMR probe at a preset temperature of 14 °C, and the kinetics of the ligand exchange was monitored as described for the preceding experiment. The results are described in the Results and Discussion and showed a first-order dependence of the rate on the PPh$_3$ concentration. Variable-temperature experiments were performed at 14, 17, 27 and 37 °C in an analogous manner, but with 40 mM substrate and 8 mM PPh$_3$ for all runs. Under no conditions was any evidence seen for the buildup of intermediates, and the reactions were quantitative within detection limits.

PPh$_3$-Catalyzed Ligand Exchange of $CpW(NCMe)_3(\eta^2\text{-}COMe)^{2+}$ (5a) in the Presence of $(CD_3)PPh_3^+I^-$. $(CD_3)PPh_3^+I^-$ was prepared from PPh$_3$ and CD$_3$I in ether. An NMR tube equipped with a ground-glass joint was loaded with **5a**(BF$_4$)$_2$ (5.0 mg, 0.0087 mmol), PPh$_3$ (2.3 mg, 0.0087 mmol), and $(CD_3)PPh_3^+I^-$ (3.5 mg, 0.0087 mmol). Acetonitrile-d_3 (0.5 mL) was added by vacuum transfer, and the tube was sealed. The ^{1}H NMR spectrum, recorded after the acetonitrile ligand exchange was complete, verified that no other reaction had taken place and that no $(CH_3)PPh_3^+$ (δ 2.79 (d, *J* = 14 Hz) had been formed.

Reaction between *cis*-$CpW(CO)_2(NCCD_3)Me$ and PPh$_3$. *cis*-$CpW(CO)_2(NCMe)Me$ was prepared in situ by the reduction of **5a**(BF$_4$)$_2$ (5.6 mg, 0.01 mmol) with cobaltocene (3.8 mg, 0.021 mmol) in acetonitrile (2.0 mL) as described previously.[10] The relative intensities of the two IR ν_{CO} absorptions at 1915 (vs) and 1815 (s) indicated the cis geometry at the metal center.[21] PPh$_3$ (2.6 mg, 0.01 mmol) was added, and the mixture was stirred for 30 min at −20 °C. The solution was transferred to an NMR tube equipped with a ground-glass joint, and the solvent was removed in vacuo. Acetonitrile-d_3 was added by vacuum transfer, the tube was sealed, and an ^{1}H NMR spectrum was recorded immediately to reveal the presence of *cis*-$CpW(CO)_2(PPh_3)Me$ (δ −0.25 (d, *J*

---

(20) Beck, W.; Schloter, K. *Z. Naturforsch. B* **1978**, *33B*, 1214.

(21) (a) Manning, A. R. *J. Chem. Soc. A* **1967**, 1984. (b) Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5852.

Organometallics **1992**, *11*, 3301–3306

= 14 Hz, 3 H), 5.34 (s, 5 H)) (ca. 80%) along with ca. 20% of the trans isomer (δ 0.42 (d, J = 2.6 Hz, 3 H), 4.87 (d, J = 1.4 Hz, 5 H)). A spectrum recorded 10 min later showed a ca 1:10 ratio of the cis and trans isomers. Phosphorus–Cp couplings are generally observed for trans, but not for cis, four-legged piano stool structures $CpM(CO)_2(PR_3)X$.[21]

Acknowledgment. We gratefully acknowledge support from Statoil under the VISTA program, administered by the Norwegian Academy of Science and Letters (stipend to V.S.), and from the Norwegian Council for Science and the Humanities, NAVF.

Note Added in Proof. The general coordination geometry of **3a** has been confirmed by an X-ray crystallographic analysis of **3a**$(PF_6)_2$ by Professor Christian Rømming. The crystal quality did not allow for an accurate structural analysis.

OM920231H

Fulvalene Derivatives of Titanium: X-ray Structures of $[(TiCl_2)_2(\mu\text{-}O)(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)]$ and $[\{Ti(CH_2C_6H_5)_3\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)]$

Luis Miguel Alvaro, Tomás Cuenca, Juan Carlos Flores, and Pascual Royo*

Departamento de Química Inorgánica, Universidad de Alcalá de Henares, Campus Universitario,
E-28871 Alcalá de Henares, Madrid, Spain

Maria Angela Pellinghelli and Antonio Tiripicchio*

Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio
per la Strutturistica Diffrattometrica del CNR, Viale delle Scienze 78, I-43100 Parma, Italy

Received March 13, 1992

Dithalliofulvalene and bis(trimethylsilyl)fulvalene were used as alkylating reagents to transfer the fulvalene group to $TiCl_4$, leading to $[(TiCl_3)_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)]$ (**1**; 30% yield). This extremely moisture-sensitive compound is quantitatively hydrolyzed to the μ-oxo dinuclear complex $[(TiCl_2)_2(\mu\text{-}O)(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)]$ (**2**) when the reaction to synthesize **1** is carried out in wet toluene or chloroform. The transformation of **2** into **1** can also be done by reacting the μ-oxo derivative with $AlEtCl_2$ in toluene. Alkylation of **1** with $[Mg(CH_2Ph)_2]\cdot THF$ led to $[\{Ti(CH_2Ph)_3\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)]$ (**3**; 97% yield). The crystal structures of **2** and **3** have been determined by X-ray diffraction methods. Crystals of **2** are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions a = 9.305 (3) Å, b = 12.387 (4) Å, c = 12.821 (4) Å, and β = 110.31 (2)°. Crystals of **3** are monoclinic, space group $P2_1/n$, with $Z = 2$ in a unit cell of dimensions a = 16.976 (6) Å, b = 11.022 (5) Å, c = 11.238 (4) Å, and β = 101.15 (2)°. Both structures were solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares on the basis of 1662 (**2**) and 2126 (**3**) observed reflections to R and R_w values of 0.0397 and 0.0482 (**2**) and 0.0490 and 0.0609 (**3**), respectively. In both compounds each fulvalene cyclopentadienyl ring is η^5-bound to one titanium atom. The remaining coordination sites of titanium are occupied by two chlorines and one bridging oxygen in **2** or by three benzyl ligands in **3**, each showing a different bonding system.

Introduction

The electron deficiency of monocyclopentadienyl complexes of the early transition metals is partially compensated by using the permethylated ring, which gives rise to similarly reactive although thermally more stable compounds. An even more reactive and structurally interesting type of complex is to be expected by using the fulvalene group, whose electron-donor capacity is lower than that of the unsubstituted cyclopentadienyl ring. Also, this $\eta^5{:}\eta^5$ bridging fulvalene group would permit the access to homo- or heterodinuclear compounds containing independent or nonindependent metal fragments. Fulvalene complexes are known for many transition metals,[1] including derivatives of group 4d elements. However, the known group 4d fulvalene complexes contain some additional cyclopentadienyl rings, being usually metallocene type compounds. A new synthetic route leading to $[(\eta^5\text{-}C_5Me_5)MCl_3]$ (M = Ti, Zr, Hf)[2a] and extended to Nb and Ta[2b,c] was developed in our laboratory by using $[(C_5Me_5)SiMe_3]$ as an alkylating agent. A variety of titanium alkyls and oxo alkyls have been synthesized previously[2d] from these starting materials, and many of these compounds show structural features that confirm the presence of electron-deficient metal centers.

The already known early-transition-metal fulvalene complexes have been previously isolated through two synthetic methods: (i) activating C–H bonds in cyclopentadienyl rings with transformations of two cyclopentadienyl units into a fulvalene group;[1] (ii) using dithalliofulvalene salts prepared by reaction of dihydrofulvalene with TlOEt.[3]

We have, previously, isolated the mono(trimethylsilyl)- and bis(trimethylsilyl)fulvalene derivatives,[4] and we report

---

(1) Wielstra, Y.; Meetsma, A.; Gambarotta, S.; Khan, S. *Organometallics* **1990**, *9*, 876 and references therein.

(2) (a) Hidalgo, G.; Mena, M.; Palacios, F.; Royo, P.; Serrano, R. *J. Organomet. Chem.* **1988**, *340*, 37. (b) Yasuda, H.; Okamoto, T.; Nakamura, A. *Organomet. Synth.* **1988**, *4*, 20. (c) De la Mata, J.; Fandos, R.; Gomez, M.; Gomez-Sal, P.; Martinez-Carrera, S.; Royo, P. *Organometallics* **1990**, *9*, 1846. (d) Gomez-Sal, P.; Mena, M.; Royo, P.; Serrano, R. *J. Organomet. Chem.* **1988**, *358*, 147.

(3) Spink, W. C.; Rausch, M. D. *J. Organomet. Chem.* **1986**, *308*, C-1.

0276-7333/92/2311-3301$03.00/0