shows two peaks at 1906 and 1768 cm^{-1} and a small peak at 2020 cm^{-1}. Likewise in this case the catalyst was poisoned for propylene metathesis. Alternatively when $Mo(CO)_6$ is reacted with the alumina from acetone solutions and activated at 100 °C, two major peaks are present in the IR spectrum at 1905 and 1771 cm^{-1} and a smaller peak is at 2036 cm^{-1}, but the material is inactive for metathesis. Thus acetone not only prevents the formation of catalytically active $Mo(CO)_3$(ads) but also poisons the active catalyst as acetonitrile did. It appears that acetone is able to coordinate to molybdenum to cause the large shifts observed in the IR spectrum as proposed for acetonitrile. Therefore the species formed in the reaction of $Mo(CO)_3(CH_3CN)_3$ with γ-alumina from acetone solution is postulated to be $Mo(CO)_3(CH_3CN)$(ads). This decomposes at elevated temperatures as evidenced by CO evolution. In addition to coordination to the molybdenum tricarbonyl acetone and acetonitrile are known to interact strongly with partially dehydroxylated surfaces, and this may also contribute to the poisoning of the metathesis activity.

The alumina-supported molybdenum carbonyls generated from $(\eta^6\text{-}C_6H_6)Mo(CO)_3$ and $Mo(CO)_6$ are indistinguishable on the basis of infrared spectroscopy and olefin metathesis activity. Thus the use of an arene ring as a leaving group is demonstrated as a viable low-temperature reaction pathway to supported metal complexes.

Acknowledgment. We thank the National Science Foundation for support of this work (DMR 85 18364).

Registry No. $(\eta^6\text{-}C_6H_6)Mo(CO)_3$, 12287-81-9; $(\eta^6\text{-}C_6H_5CH_3)Mo(CO)_3$, 12083-34-0; $Mo(CO)_6$, 13939-06-5; $Mo(CO)_3(CH_3CN)_3$, 15038-48-9; propylene, 115-07-1.

Synthesis and Crystal and Molecular Structures of $M(OAr')_2(CH_2\text{-py-6Me})_2$ (M = Hf, Th; OAr′ = 2,6-Di-*tert*-butylphenoxide; CH_2-py-6Me = 2-(6-Methylpyridyl)methyl), Complexes Containing Two C,N-Chelating Pyridyl–Methyl Ligands

Sharon M. Beshouri, Phillip E. Fanwick, and Ian P. Rothwell*[1]

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

John C. Huffman

Molecular Structure Center, Indiana University, Bloomington, Indiana 47405

Received March 2, 1987

The reaction of the tetrachlorides MCl_4 (M = Hf, Th) with excess of $LiCH_2$-py-6Me ($LiCH_2$-py-6Me = (2-(6-methylpyridyl)methyl)lithium) leads to the sparingly soluble dialkyls $MCl_2(CH_2\text{-py-6Me})_2$ (M = Hf, Th). Further treatment of these materials with LiOAr′ (>2 equiv; OAr′ = 2,6-di-*tert*-butylphenoxide) leads to the pale yellow, crystalline compounds $M(OAr')_2(CH_2\text{-py-6Me})_2$ (M = Hf, Th) which are soluble in hydrocarbon solvents and are more amenable to study. Structural studies show both the hafnium and thorium compounds to be isomorphous and isostructural, the metal being found to be six-coordinate with both pyridyl–methyl ligands C,N-chelating. Some distortions of the coordination environment are evident, presumably due to the formation of two strained, four-membered rings. Although the M–N(py) distances do not appear to be elongated, solution studies indicate that dissociation of pyridine groups is facile. However, ^{13}C NMR data are supportive of the idea that the ligands remain predominantly, C,N-bound in solution. $Hf(OAr')_2(CH_2\text{-py-6Me})_2$ crystallizes in space group $I2/a$ with a = 16.980 (4) Å, b = 10.438 (1) Å, c = 21.865 (5) Å, β = 106.77 (1)°, Z = 4, and d_{calcd} = 1.435 g cm^{-3} at −157 °C. $Th(OAr')_2(CH_2\text{-py-6Me})_2$ also crystallizes in space group $I2/a$ with a = 16.826 (5) Å, b = 10.679 (1) Å, c = 22.491 (5) Å, β = 106.04 (2)°, Z = 4, and d_{calcd} = 1.462 g cm^{-3} at 22 °C.

Introduction

The ability of donor ligands and solvents to stabilize high-valent early-transition-metal homoleptic alkyl compounds was recognized by early synthetic workers in this branch of organometallic chemistry.[2,3] Hence thermally unstable, even sometimes explosive, peralkyls can be stabilized by chelating ligands such as bpy and dmpe.[4] The field of cyclometalation chemistry which has developed over the last 20 years owes much to the enhanced stability imparted to the metal–carbon bond formed in these reactions by the heteroatom donor in the resulting metallacycle.[5–7] Work by Manzer[8] and others[9] has demonstrated

---

(1) (a) Camille and Henry Dreyfus Teacher-Scholar, 1985–1990. (b) Fellow of the Alfred P. Sloan Foundation, 1986–1990.

(2) Wilkinson, G., *Science (Washington, DC)* **1974**, *185*, 109.

(3) (a) Davidson, P. J.; Lappert, M. F.; Pearce, R. *Chem. Rev.* **1976**, *76*, 219. (b) Schrock, R. R.; Parshall, G. W. *Chem. Rev.* **1976**, *76*, 243.

(4) (a) Zucchini, V.; Albizzati, E.; Giannini, V. *J. Organomet. Chem.* **1971**, *26*, 357. (b) Edwards, P. G.; Andersen, R. A.; Zalkin, A. *Organometallics* **1984**, *3*, 293.

(5) (a) Dehand, J.; Pfeffer, M. *Coord. Chem. Rev.* **1976**, *18*, 326. (b) Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73.

(6) (a) Webster, D. E. *Adv. Organomet. Chem.* **1977**, *15*, 147. (b) Shilov, A. E.; Shteinman, A. A. *Coord. Chem. Rev.* **1977**, *24*, 97. (c) Parshall, G. W. *Catalysis* **1977**, *1*, 335. (d) Parshall, G. W. *Acc. Chem. Rev.* **1975**, *8*, 113.

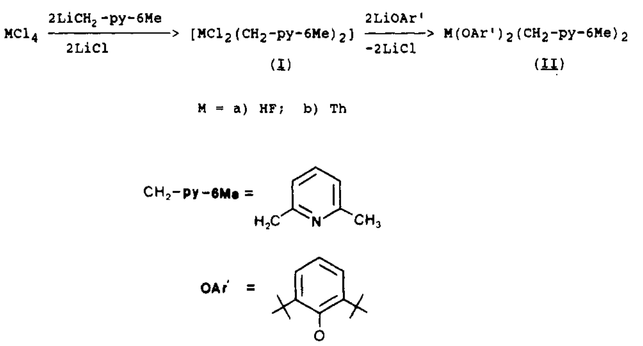
(7) Rothwell, I. P. *Polyhedron* **1985**, *4*, 177.

(8) (a) Manzer, L. E. *J. Am. Chem. Soc.* **1978**, *100*, 8068. (b) Manzer, L. E. *Inorg. Chem.* **1978**, *17*, 1552. (c) Manzer, L. E. *J. Organomet. Chem.* **1977**, *135*, C6. (d) Manzer, L. E. *Inorg. Chem.* **1976**, *15*, 2567.

(9) (a) Shore, N. E.; Hope, H. *J. Am. Chem. Soc.* **1980**, *102*, 4251. (b) Shore, N. E.; Young, S. J.; Olmstead, M. M.; Hofmann, P. *Organometallics* **1983**, *2*, 1769.

0276-7333/87/2306-2498$01.50/0 © 1987 American Chemical Society

Scheme I



that the use of functionalized alkyl and aryl ligands can lead to more stable early-transition-metal alkyl derivatives. An interesting example of this stabilization of metal–carbon σ-bonds by electron donation is seen in the increased stability of homoleptic benzyl compounds over their simpler alkyl counterparts.[10] This is a consequence of the ability of the benzyl ligand to distort so as to allow the π-cloud of the aromatic ring to donate electron density to the metal. The resulting bonding mode has been structurally characterized and contains acute M–CH_2–Ph angles sometimes as small as 85°. Similarities with the later transition-metal η^3-benzyl ligands such as in CpMo$(CO)_2(\eta^3\text{-}CH_2Ph)$[11] have been noted although a more extensive multisite interaction between the metal and aromatic π-cloud has been proposed in some cases.[12]

Our studies of the early-transition-metal organometallic chemistry associated with benzyl ligands has prompted us to investigate the chemistry of the related, functionalized ligand 2-(6-methylpyridyl)methyl, CH_2-py-6Me. The presence of the nitrogen donor atom in the aromatic ring makes available a number of possible bonding modes, some of which have been demonstrated by other workers.[13,14] In this paper we wish to report the synthesis, structure, and spectroscopic properties of two derivatives of this group containing the sterically bulky aryloxide ligand. 2,6-Di-*tert*-butylphenoxide (OAr′) for direct comparison with the previously reported benzyl analogues.[15] We have previously communicated the synthesis, structure, and reactivity of the compounds $Cp_2M(CH_2\text{-py-6Me})_2$ (M = Zr, Hf).[16]

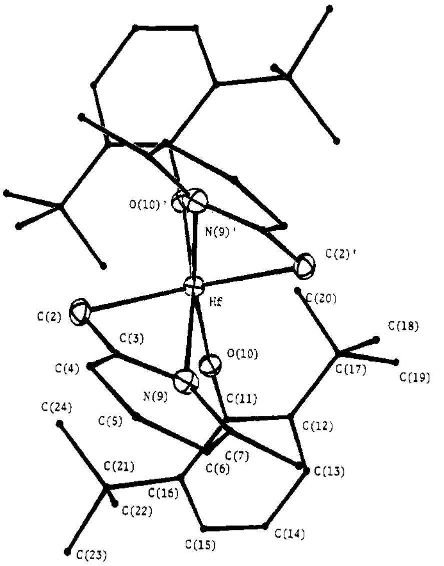


Figure 1. ORTEP view of $Hf(OAr')_2(CH_2\text{-py-6Me})_2$ (IIa) emphasizing the central coordination sphere and looking down the crystallographically imposed C_2 axis.

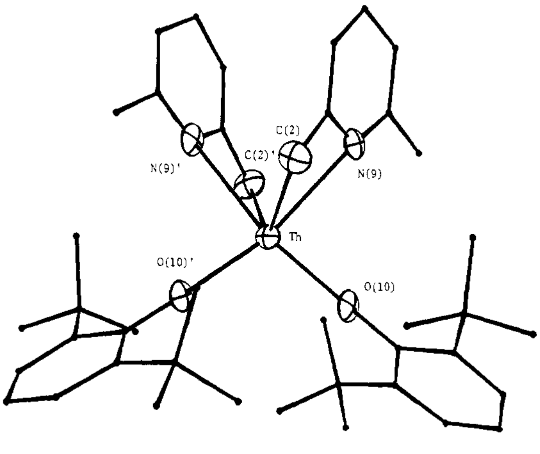


Figure 2. ORTEP view of $Th(OAr')_2(CH_2\text{-py-6Me})_2$ (IIb). The labeling scheme is identical with that used for IIa.

Table I. Fractional Coordinates and Isotropic Thermal Parameters for $Hf(OAr')_2(CH_2\text{-py-6Me})_2$ (IIa)

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Hf(1)	7500*	520.6 (3)	5000*	11
C(2)	8684 (3)	9447 (6)	4992 (3)	16
C(3)	8495 (3)	−1628 (5)	5370 (2)	15
C(4)	8707 (3)	−2909 (5)	5385 (3)	19
C(5)	8492 (3)	−3704 (6)	5815 (3)	22
C(6)	8064 (4)	−3229 (6)	6215 (3)	23
C(7)	7823 (3)	−1958 (5)	6161 (2)	17
C(8)	7384 (5)	−1353 (8)	6590 (4)	31
N(9)	8011 (2)	8813 (4)	5723 (2)	15
O(10)	7183 (2)	1731 (3)	4262 (2)	14
C(11)	7017 (3)	2476 (5)	3722 (2)	14
C(12)	6208 (3)	2557 (5)	3284 (2)	16
C(13)	6103 (4)	3277 (6)	2733 (3)	19
C(14)	6733 (3)	3919 (6)	2589 (3)	20
C(15)	7502 (4)	3879 (5)	3023 (3)	20
C(16)	7667 (3)	3204 (5)	3594 (2)	17
C(17)	5445 (3)	1857 (5)	3374 (2)	19
C(18)	5558 (4)	402 (6)	3307 (3)	26
C(19)	4646 (4)	2209 (8)	2857 (3)	29
C(20)	5297 (4)	2202 (7)	4009 (3)	22
C(21)	8533 (3)	3347 (5)	4068 (3)	18
C(22)	8994 (3)	2063 (6)	4168 (3)	19
C(23)	9082 (4)	4291 (7)	3834 (3)	26
C(24)	8458 (4)	3908 (6)	4697 (3)	20

Results and Discussion

The addition of ≥2 equiv of $LiCH_2$-py-6Me ($LiCH_2$-py-6Me = 2-(6-methylpyridyl)methyllithium) to the tetrahalides MCl_4 (M = Hf, Th) in diethyl ether leads to the formation of the sparingly soluble dichlorides $[MCl_2(CH_2\text{-py-6Me})_2]$ (M = Hf, Ia; M = Ib). Attempts to further substitute the two remaining chlorides with $LiCH_2$-py-6Me proved difficult and so far has failed to produce any tractable products. The low solubility of I and contami-

---

(10) (a) Davies, G. R.; Jarvis, J. A.; Kilbourn, B. T. *J. Chem. Soc., Chem. Commun.* **1971**, 1511. (b) Davies, G. R.; Jarvis, J. A.; Kilbourn, B. T.; Pioli, A. J. *J. Chem. Soc., Chem. Commun.* **1971**, 677.

(11) Cotton, F. A.; LaPrade, M. D. *J. Am. Chem. Soc.* **1968**, *90*, 5418.

(12) Mintz, E. A.; Moloy, K. G.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 4692.

(13) (a) Onishi, M.; Hiraki, K.; Maedra, K.; Itoh, T. *J. Organomet. Chem.* **1980**, *188*, 245. (b) Nakatsu, K.; Krafuku, K.; Yamaokra, K.; Isobe, Y.; Nakramura, Y.; Krawaguchi, S. *Inorg. Chim. Acta* **1981**, *54*, L69. (c) Onishi, M.; Hiraki, K.; Itoh, T.; Ohrama, Y. *J. Organomet. Chem.* **1983**, *254*, 381.

(14) (a) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Rothwell, I. P. *Inorg. Chem.* **1981**, *20*, 2215. (b) Henderson, M. J.; Papasergio, R. I.; Rastan, C. L.; White, A. H.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1986**, 672. (c) Bailey, S. I.; Colgan, D.; Engelhardt, L. M.; Leung, W. P.; Papasergio, R. I.; Rastan, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1986**, 603. (d) Colgan, D.; Papasergio, R. I.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1984**, 1708.

(15) Latesky, S. L.; McMullen, A. K.; Niccolai, G. P.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1985**, *4*, 902.

(16) Beshouri, S. M.; Fanwick, P. E.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1987**, *6*, 891.

Table II. Fractional Coordinates and Isotropic Thermal Parameters for $Th(OAr')_2(CH_2\text{-py-6Me})_2$ (IIb)[a]

atom	x	y	z	B, Å^2
Th	3/4	0.06578 (8)	1/2	2.10 (1)
O(10)	0.7156 (6)	0.1900 (9)	0.4195 (4)	2.9 (2)
N(9)	0.8108 (7)	−0.119 (1)	0.5742 (5)	3.0 (3)
C(2)	0.8789 (9)	−0.061 (2)	0.5010 (7)	3.3 (3)
C(3)	0.8552 (9)	−0.160 (1)	0.5367 (7)	3.0 (4)
C(4)	0.871 (1)	−0.289 (1)	0.5327 (9)	4.3 (4)
C(5)	0.844 (1)	−0.374 (2)	0.5722 (9)	4.7 (5)
C(6)	0.808 (1)	−0.320 (2)	0.6147 (9)	5.5 (5)
C(7)	0.789 (1)	−0.196 (2)	0.6146 (8)	4.1 (4)
C(8)	0.747 (1)	−0.136 (2)	0.6590 (8)	5.1 (5)
C(11)	0.700 (1)	0.265 (1)	0.3675 (6)	2.9 (4)
C(12)	0.6189 (9)	0.273 (1)	0.3267 (7)	2.7 (3)
C(13)	0.609 (1)	0.347 (2)	0.2748 (8)	4.4 (5)
C(14)	0.673 (1)	0.410 (2)	0.2600 (8)	5.0 (5)
C(15)	0.751 (1)	0.400 (2)	0.2999 (8)	4.3 (4)
C(16)	0.7665 (8)	0.331 (1)	0.3540 (7)	2.6 (3)
C(17)	0.542 (1)	0.210 (2)	0.3372 (8)	4.0 (4)
C(18)	0.549 (1)	0.065 (2)	0.3292 (8)	4.5 (4)
C(19)	0.461 (1)	0.248 (2)	0.287 (1)	6.3 (5)
C(20)	0.529 (1)	0.244 (2)	0.3985 (8)	4.6 (5)
C(21)	0.8526 (9)	0.330 (2)	0.3982 (7)	3.4 (4)
C(22)	0.892 (1)	0.197 (2)	0.4100 (8)	4.1 (4)
C(23)	0.913 (1)	0.413 (2)	0.375 (1)	7.1 (6)
C(24)	0.849 (1)	0.392 (2)	0.462 (1)	5.2 (5)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table III. Selected Bond Distances (Å) and Angles (deg) for $M(OAr')_2(CH_2\text{-py-6Me})_2$ (M = Hf, IIa; M = Th, IIb)

	M = Hf	M = Th
	Bond Distances	
M–O(10)	1.996 (3)	2.190 (9)
M–N(9)	2.374 (4)	2.61 (1)
M–C(2)	2.307 (5)	2.55 (1)
	Bond Angles	
O(10)–M–O(10)′	101.4 (2)	105.4 (4)
–N(9)	88.6 (1)	87.9 (3)
–C(2)	109.5 (2)	111.0 (4)
N(9)–M–N(9)′	87.2 (2)	81.4 (5)
–C(2)′	59.3 (2)	53.8 (4)
C(2)M–C(2)′	121.9 (3)	115.8 (6)
M–O(10)–C(11)	173.4 (3)	175.4 (9)
M–C(2)–C(3)	91.9 (3)	91.6 (8)
M–N(9)–C(3)	92.3 (3)	91.6 (9)
M–N(9)–C(7)	143.1 (3)	139 (1)

Table IV. Crystal Structure Determination Data

	IIa	IIb
formula	$HfC_{42}H_{58}N_2O_2$	$ThC_{42}H_{58}N_2O_2$
fw	801.42	854.98
space group	*I*2/*a*	*I*2/*a*
a, Å	16.980 (4)	16.826 (5)
b, Å	10.438 (1)	10.679 (1)
c, Å	21.865 (5)	22.491 (5)
α, deg	90	90
β, deg	106.77 (1)	106.04 (2)
γ, deg	90	90
Z	4	4
V, Å^3	3710.49	3884.0
d(calcd), g/cm^3	1.435	1.462
cryst size	0.20 × 0.18 × 0.10	0.33 × 0.31 × 0.13
cryst color	yellow	yellow
radiatn	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)
linear abs coeff, cm^{-1}	28.211	
temp, °C	−157	+22
detector aperture	3.0 mm wide × 4.0 mm high	(1.5 + tan γ) mm wide × 4.0 mm high
takeoff angle, deg	2.0	4.90
scan speed, deg/min	4.0	variable
scan width, deg	2.0 + dispersion	0.8 + 0.35 tan γ, 50% of scan time
bkgd counts, s	8	
2θ range, deg	6–45	4–50
unique data	2421	2688
unique data with $F_o > 3.00\sigma$	2256	1899
R(*F*)	0.0272	0.058
$R_w(F)$	0.0280	0.077
goodness of fit	0.815	1.507
largest Δ/σ	0.05	0.11

nation with LiCl precluded their full characterization. However, the addition of LiOAr′ (≥2 equiv, OAr′ = 2,6-di-*tert*-butylphenoxide) to ether suspensions of I led to the hydrocarbon-soluble, pale yellow derivatives $M(OAr')_2(CH_2\text{-py-6Me})_2$ (M = Hf IIa; M = Th, IIb) in good yields (Scheme I). Attempts to prepare the zirconium and titanium analogues of II have so far been unsuccessful. The dichloride compound $[ZrCl_2(CH_2\text{-py-6Me})_2]$ proved to be thermally unstable while addition of $LiCH_2$-py-6Me to $TiCl_4$ appears to result in reduction of the metal. Both IIa and IIb can be readily recrystallized from hexane as large flat plates and both were subjected to an X-ray diffraction analysis.

Solid-State and Molecular Structures of $M(OAr')_2(CH_2\text{-py-6Me})_2$ (M = Hf, Ia; M = Th, IIb). The two materials were found to be isomorphous. Figures 1 and 2 show two different views of the isostructural compounds while Tables I and II contain the fractional coordinates and isotropic thermal parameters for IIa and IIb, respectively. Table III contains a comparison of some selected bond distances and angles. The molecules contain a crystallographically imposed C_2 axis making the aryloxides and the two pyridyl–methyl ligands equivalent. It can be seen that both of the pyridyl–methyl ligands are C,N-bound resulting in a six-coordinate metal center. This contrasts with the situation for $Cp_2Zr(CH_2\text{-py-6Me})_2$ where one mono- and one bidentate pyridyl–methyl ligand were observed. However, the coordination environment is not best described as octahedral in compounds II. The structure bears a close relationship to that found for the bis(iminoacyl) complex $(Ar'O)_2Hf(\eta^2\text{-PhNCMe})_2$[17] and contrasts with the bis(benzyl) complex $(Ar'O)_2Zr(CH_2Ph)_2$ where both benzyls were found to be purely σ-bound. It would appear from both structures that the two oxygen and two carbon atoms mutually form a pseudotetrahedral environment about the metal. The remaining nitrogen atoms then bend in to coordinate at positions approximately trans to the oxygen atoms. The resulting coordination environment can also be approximated to a trigonal prism, the triangular faces being formed by O, C, and N atoms.

The coordination of the 2,6-di-*tert*-butylphenoxide groups appears typical for these ligands, containing short M–O distances and large M–O–Ar′ angles.[18] However, the structural characteristics of the pyridyl–methyl ligands are certainly worthy of detailed discussion. The $M-(CH_2\text{-py-6Me})$ distances of 2.307 (5) (M = Hf) and 2.55 (1) Å (M = Th) compare favorably with the $M-CH_2Ph$ distances of 2.243 (9) and 2.272 (8) Å in $Zr(OAr')_2(CH_2Ph)_2$[15] and 2.58 (2) Å in $CpTh(CH_2Ph)_3$.[12] Hence the pyridyl group

---

[17] Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L.; Latesky, S. L.; McMullen, A. K., Rothwell, I. P.; Folting, K.; Huffman, J. C.; Streib, W. E.; Wang, R. *J. Am. Chem. Soc.* **1987**, *109*, 390.

[18] Fanwick, P. E.; Ogilvy, A. E.; Rothwell, I. P. *Organometallics* **1987**, *6*, 73 and references therein.

does not appear to cause a significant change in M–CH_2 distances compared to benzyl analogues. The M–N(py) distances of 2.374 (6) Å (M = Hf) and 2.61 (1) Å (M = Th) are both longer than the M–C distances. However, despite the presence of the strained four-membered metallacycle ring, the distances do not appear to be significantly different than would be predicted for normal pyridine coordination to these types of metal centers. Compare with the Zr–py distance of 2.403 (1) Å in $Cp_2Zr(\eta^2\text{-}H_2C{=}CO)(py)$.[19] The difference in M–C and M–N distances on goining from IIa to IIb, +0.24 Å, contrasts with the much smaller increase in M–OAr′ distances (+0.094 Å). We attribute the relatively shorter Th–O distance to increased oxygen p to metal π-bonding.

It is perhaps surprising that the M–N and M–C distances appear normal in view of the distortions associated with the four-membered metallacycle. The M–C–py angle is reduced to 92° (vide infra) while the bite of the chelate is only 59° and 54°, respectively, for IIa and IIb. However, one distortion that is noticeable about the pyridine coordination concerns the fact that the metal atom lies considerably out of the plane of the pyridine ring. Normal pyridine coordination in which the nitrogen lone-pair, metal overlap is maximized would involve the metal and heterocyclic ring atoms lying coplanar. Previous work on quinoline and biquinolyl ligands coordinated to later transition metals has shown that this type of deformation can readily take place in order to relieve steric pressure at the metal center, without necessarily causing a dramatic decrease in pyridine–metal bonding.[20,21] In molecules I it can be seen that this distortion leads to a decrease in any possibly unfavorable steric interactions between the 6-methyl substituent and the rest of the coordination sphere.

Spectroscopic Properties. The solid-state structure of Ia and Ib indicate both CH_2-py-6Me ligands to be equivalent. Solution spectra of compounds I also indicate only one type of ligand as evidenced by only one set of ^1H and ^{13}C NMR signals attributable to this group. However, the solid-state structures of I predict the methylene protons of the CH_2-6Me group will be diastereotopic, resulting in an AB pattern in the ^1H NMR spectrum. However, these methylene protons remain as a sharp singlet even down to −70 °C in toluene-d_8 solvent. There are three plausible explanations for these observations. (i) In solution the pyridyl–methyl ligands are only C-bound so that a structure analogous to $(Ar'O)_2Zr(CH_2Ph)_2$ is adopted. (ii) The solution structure maintains C,N-chelating pyridylmethyl groups, but a different coordination geometry is adopted in which the methylene protons are equivalent. (iii) An identical structure is maintained in solution, but the pyridyl–methyl ligands undergo rapid dissociation and recoordination of the nitrogen atoms allowing facile interchange of the two possible enantiomers.

Although it is not possible to conclusively differentiate these three possibilities, the ^{13}C NMR data appear to be consistent with the pyridyl–methyl groups remaining C,N-bound in solution. The most critical data in the argument involves the $^1J(^{13}C\text{–}^1H)$ coupling constant for the CH_2-py-6Me group. For the simple, saturated cyclic hydrocarbons $(CH_2)_n$ the value of this parameter increases with decreasing ring size, ranging from 123 Hz for cyclohexane to 161 Hz for cyclopropane.[22] In the case of the compounds in this study, solution measurements give rise to values of 146 and 139 Hz for the CH_2-py-6Me coupling constants for IIa and IIb, respectively. This value is too large for an unstrained methylene group and compares favorably with the 134-Hz coupling constant reported for cyclobutane.[23] Hence on this evidence it appears that the pyridyl-methyl ligands remain chelated (M–C–py ≃ 92°) in solution. A correlation between the $^1J(^{13}C\text{-}^1H)$ values of the methylene groups of benzyl ligands and the observed solid-state M–CH_2–Ph angles has previously been observed.[15] Spectroscopic data for compounds containing only C-bound CH_2-py-6Me ligands indicate coupling constants of 120–125 Hz for the methylene group, again consistent with this argument.[16]

Experimental Section

All reactions and manipulations were carried out under N_2 by using a Vacuum Atmospheres drybox and conventional Schlenk techniques. Solvents were dried by distillation over Na/benzophenone under N_2. Metal chloride compounds were purchased in resublimed form from Alfa and Aldrich. ^1H NMR spectra were recorded by using Perkin-Elmer R-32 90 MHz and Varian XL 200 NMR spectrometers while ^{13}C spectra were recorded by using a Varian XL 200 NMR instrument.

Preparation of $LiCH_2$-py-$6CH_3$. A solution of 2-6-dimethylpyridine (50 mL, 4.29 × 10^{-1} mol) in 400 mL of hexane was stirred and cooled in an ice-water bath; Li*n*-Bu (2.4 M, 165 mL, 4.29 × 10^{-1} mol) was added slowly via syringe. Upon completion of addition an orange precipitate formed. The flask was gradually warmed to room temperature when the reaction mixture was filtered. The yellow salt was washed with hexane (3 × 30 mL) then thoroughly dried under vacuum.

Preparation of $Hf(OAr')_2(CH_2$-py-$6Me)_2$ (IIa). A suspension of $HfCl_4$ (2.0 g) in diethyl ether (50 mL) was stirred vigorously at room temperature while a solution of $LiCH_2$-py-6Me (2.2 equiv) in ether was added slowly. The mixture was stirred for 1 h. The resulting suspension of the dichloride $HfCl_2(CH_2\text{-py-}6Me)_2$ was then treated with a suspension of LiOAr′ (2.2 equiv) in diethyl ether. The mixture was then stirred for 18 h before the solvent was removed under vacuum and the resulting solids were extracted with 200 mL of hexane. When this solution was concentrated and cooled, the product was obtained as large yellow plates, yield 1.2 g (25%). Anal. Calcd for $HfC_{42}H_{58}N_2O_2$: C, 62.95; H, 7.29; N, 3.50. Found: C, 62.77; H, 7.35; N, 3.27. ^1H NMR (C_6D_6, 30 °C): δ 1.61 (s, OAr′-*t*-*Bu*), 2.09 (s, CH_2-py-6Me), 2.41 (s, CH_2-py-6*Me*), 6.0–7.4 (m, aromatics). ^{13}C NMR (C_6D_6, 30 °C): δ 24.5 (CH_2-py-6CH_3), 63.8 (CH_2-py-6Me, ^1J = 145 Hz).

Preparation of $Th(OAr')_2(CH_2$-py-$6Me)_2$ (IIb). A procedure essentially identical with that used for IIa yielded IIb as yellow plates, yield 1.4 g from 2.0 g of $ThCl_4$ (30%). ^1H NMR (C_6D_6, 30 °C): δ 1.65 (s, OAr′-*t*-*Bu*), 2.30 (s, CH_2-py-6*Me*), 2.76 (CH_2-py-6Me). ^{13}C NMR (C_6D_6, 30 °C): δ 30.4 (CH_2-py-6*Me*), 64.0 (CH_2-py-6Me, ^1J = 139 Hz).

X-ray Structure Determinations. Crystal Structure Determination Data Are Collected in Table IV. $Hf(OAr')_2(CH_2$-py-$6Me)_2$ (IIa). A suitable crystal was located and transferred to the goniostat by using standard inert-atmosphere handling techniques employed by the Indiana University Molecular Structure Center[23] and cooled to −155 °C for characterization and data collection.

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with systematic extinctions and symmetry corresponding to an *I*-centered monoclinic cell. Since the β angle became acute when the cell was transformed to a normal centered cell, the *I*-centered choice was utilized.

Data were collected in the usual manner using a continuous γ–2γ scan technique. Data were reduced in the usual manner.[23] The structure was solved by a combination of direct methods

---

(19) Moore, E. J.; Straus, D. A.; Armantrout, J.; Santasiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2068.

(20) Deeming, A. J.; Rothwell, I. P.; Hursthouse, M. B.; Backer-Dirks, J. D. J. *J. Chem. Soc., Chem. Commun.* **1979**, 670.

(21) Newkome, G. R.; Fronczek, F. R.; Gupta, V. K.; Puckett, W. E.; Pantaleo, D. C.; Kiefer, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 1982.

(22) Silverstein, R. M.; Baxler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1900; p 273.

(23) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

(MULTAN78) and Fourier techniques and refined by full-matrix least squares. Hydrogen atoms were visible in a Fourier phased on the non-hydrogen parameters and were included in the final cycles. Non-hydrogen atoms were assigned anisotropic thermal parameters while hydrogens were allowed to vary isotropically. A ψ scan of a reflection located at ca. $\chi = 90°$ indicated a fluctuation of over 10%, so an absorption correction was applied.

A final difference Fourier was essentially featureless, with the largest peak being 0.50 e/A^3, other than one peak located at the Hf site which was 1.04 e/A^3.

$Th(OAr')_2(CH_2$-py-6Me$)_2$ (IIb). A suitable crystal was located and mounted in a 0.5-mm capillary surrounded by epoxy resin. Data collection and refinement were carried out by using the standard procedures of the Purdue Crystallographic facility.

Hydrogen atoms were located such that the hydrogen–carbon bond was 0.95 Å and the angles were correct. For methyl groups, one hydrogen was located in the Fourier map, its position was idealized, and the remaining hydrogen positions were calculated on the basis of it. Hydrogen temperature factors and positions were not refined.

The absorption in these crystals was very large. This was not helped by the fact that they were large plates. All ψ scan sets displayed positions where the diffracted beam disappeared. Attempts to base corrections on these ψ scans were not successful.

Acknowledgment. We thank the National Science Foundation (Grant CHE-8612063 to I.P.R.) for support of this research. We also thank the National Science Foundation Chemical Instrumentation Program (Grant CHE-8204994) for support of the X-ray diffraction facility at Purdue. I.P.R. also gratefully acknowledges the Camille and Henry Dreyfus Foundation for the award of a Teacher-Scholar Grant and the Alfred P. Sloan Foundation for a fellowship.

Registry No. Ia, 110527-86-1; Ib, 110527-88-3; IIa, 110527-87-2; IIb, 110527-89-4; $LiCH_2$-py-6-CH_3, 34667-18-0; LiOAr′, 55894-67-2; $HFCl_4$, 13499-05-3; $ThCl_4$, 10026-08-1; 2,6-dimethylpyridine, 108-48-5.

Supplementary Material Available: Tables of positional parameters, general temperature factors, bond distances, and bond angles (13 pages); listings of structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

Synthesis of Triangular Mixed-Metal Clusters by the Addition of Copper Electrophiles to an Electron-Rich Rhodium–Rhodium Bond. X-ray Crystal Structures of $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)(\mu\text{-}CuI)]$ and $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)(\mu\text{-}AgO_2CCH_3)]$

Giuseppe Bruno, Sandra Lo Schiavo, Enrico Rotondo, Pasquale Piraino, and Felice Faraone*

Dipartimento di Chimica Inorganica e Struttura Molecolare, Università di Messina, Piazza S. Pugliatti,
98100 Messina, Italy

Received March 23, 1987

The new Rh_2Cu mixed-metal clusters $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}CuX)]$ (X = Cl, **2**; X = I, **3**; dppm = bis(diphenylphosphino)methane) have been prepared by reacting $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})]$ (**1**) with CuX and have been spectroscopically characterized. The structure of **3** has also been established by X-ray crystallography. The compound crystallizes in the orthorhombic space group *Pnma* with a = 14.002 (2) Å, b = 18.306 (2) Å, c = 13.025 (1) Å, V = 3338.5 Å^3, and Z = 4. The structure has been refined to R = 0.034 and R_w = 0.039 for the 1064 reflections with $I \geq 3\sigma(I)$. Complex **3** reacts with AgO_2CCF_3 to yield $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}AgO_2CCF_3)]$ (**4**) which has been structurally characterized. Crystals of **4** are also orthorhombic of space group *Pnma* with a = 15.133 (2) Å, b = 18.176 (3) Å, c = 12.656 (1) Å, V = 3481.0 Å^3, and Z = 4. R = 0.034 and R_w = 0.034 for the 1993 reflections with $I \geq 3\sigma(I)$. In both complexes structurally characterized the three metal atoms define a triangular cluster [in **3** Rh(1)–Rh(1′) = 2.746 (1), Rh(1)–Cu = 2.588 (2) Å; in **4** Rh(1)–Rh(1′) = 2.776 (1), Rh(1)–Ag = 2.719 (1) Å] with the Rh–Rh bond bridged by the dppm and the CO ligands. The rhodium atoms are each symmetrically capped by one η-cyclopentadienyl ligand, and the interplanar angle between the cyclopentadienyl rings can be related to the bulk of the group 11 metal. In **3** the iodine atom is bonded to copper while in **4** the trifluoroacetate group is chelated to the silver atom. The structural features of **3** and **4** have been compared with those of the other compounds of this class already reported. The results show that the formation of stable Rh_2Ag and Rh_2Cu triangular clusters by addition of electrophiles containing the group 11 metals to **1** requires the use of silver or copper salts of coordinating anions.

Introduction

We recently reported the synthesis and the X-ray structural characterization of mixed-metal clusters in which a group 11 atom, Au or Ag, is part of a triangular cluster.[1-4] These species, $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}AuPPh_3)]X$, $[Rh_2Ag(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})]X$ (X = BF_4, PF_6), and $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}AgY)]$ (Y = O_2PF_2, O_2CCH_3, O_2CCF_3, S_2PEt_2), were obtained by addition of silver or gold electrophiles to the electron-rich rhodium–rhodium bond of $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})]$ (**1**) (dppm = bis(diphenylphosphino)methane).

In this paper we describe the synthesis of the analogous copper derivatives $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-dppm})(\mu\text{-}CuX)]$

---

(1) Faraone, F.; Bruno, G.; Lo Schiavo, S.; Bombieri, G. *J. Chem. Soc., Dalton Trans.* **1984**, 533.

(2) Bruno, G.; Lo Schiavo, S.; Piraino, P.; Faraone, F. *Organometallics* **1985**, *4*, 1098.

(3) Lo Schiavo, S.; Bruno, G.; Nicolò, F.; Piraino, P.; Faraone, F. *Organometallics* **1985**, *4*, 2091.

(4) Lo Schiavo, S.; Bruno, G.; Piraino, P.; Faraone, F. *Organometallics* **1986**, *5*, 1400.

0276-7333/87/2306-2502$01.50/0