

HRh(CO)₂[η²-MeC(CH₂PPh₂)₃] (2), containing a free phosphine arm (Scheme I).

The exact coordination mode of the triphos ligand in 2 was established by high-pressure NMR spectroscopy. The ³¹P NMR spectrum of 1 (0.05 mmol) in 1.8 g of THF-*d*₆ shows a doublet at 18 ppm (*J*_{Rh-P} = 118 Hz; Figure 2), indicating three chemically equivalent -CH₂PPh₂ arms bonded to rhodium.^{2d} When the solution was charged with 450 psi of H₂/CO (1:1), the intensity of the doublet decreased and two new resonances appeared (Figure 2), a doublet at 15.9 ppm (*J*_{Rh-P} = 113 Hz) and a singlet at -26.8 ppm, with relative intensities of 2:1, respectively. These resonances are assigned to an η²-MeC(CH₂PPh₂)₃ ligand in 2, which has one -CH₂PPh₂ arm not bonded to the rhodium. When the pressure was increased to 900 psi, the relative intensity of the doublet at 18.0 ppm further decreased and the intensity of the resonance assigned to η²-MeC(CH₂PPh₂)₃ proportionally increased. Measurements of the equilibrium between 1 and 2 are in progress.

In conclusion, we have established by high-pressure IR and NMR spectroscopy that the tripodal ligand MeC(CH₂PPh₂)₃ can readily undergo reversible dissociation of one of its phosphine arms under hydroformylation conditions. The arm-off dissociation can rationalize the low *n*/*i* selectivities frequently observed in the catalytic hydroformylation of olefins using triphos-modified rhodium catalysts.^{2a,6} The coordination of the η²-MeC(CH₂PPh₂)₃ ligand to rhodium is similar to that of η²-Ph₂P(CH₂)₃PPh₂, and bis(diphenylphosphino)alkane-modified rhodium hydroformylation catalysts are known to give low *n*/*i* ratios.⁷

Acknowledgment. The very careful technical work by Raymond A. Cook is gratefully acknowledged.

(6) Our results on the hydroformylation of hexene-1 at 100 °C and 450 psi of H₂/CO pressure using 1 as catalyst were very similar to those reported by Bianchini and co-workers.^{2a}

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Approaches to Hexane-Soluble Cationic Organometallic Lewis Acids. Synthesis, Structure, and Solubility of Titanium Complexes of the Formula [(η⁵-C₅(Si(CH₃)₃)_nH_{5-n})Ti(acac)₂]⁺OTf⁻ (n = 2, 3)

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Summary: Treatment of (1,3-bis(trimethylsilyl)cyclopentadienyl)titanium trichloride with silver triflate (1 equiv) and acetylacetonate RCOCH₂COR (2 equiv, R = CH₃, ^tBu, CF₃) in dichloromethane affords the triflate complexes [(1,3-C₅(Si(CH₃)₃)₂H₃)Ti(CH₃COCHCOCH₃)₂]⁺TfO⁻, [(1,3-C₅(Si(CH₃)₃)₂H₃)Ti(^tBuCOCHCO^tBu)₂]⁺TfO⁻, and [(1,3-C₅(Si(CH₃)₃)₂H₃)Ti(CF₃COCHCOCF₃)₂OTf]. Similar reactions using (1,2,4-tris(trimethylsilyl)cyclopentadienyl)titanium trichloride and RCOCH₂COR (R = ^tBu, CF₃) give [(1,2,4-C₅(Si(CH₃)₃)₃H₂)Ti(^tBuCOCHCO^tBu)₂]⁺TfO⁻ and [(1,2,4-C₅(Si(CH₃)₃)₃H₂)Ti(CF₃COCHCOCF₃)₂OTf]. These complexes exhibit modest to excellent solubility in alkane and perfluoroalkane solvents and demonstrate that ionic complexes can be solubilized into even the most nonpolar solvents with the appropriate choice of ligands. The ionic versus molecular nature of the complexes has been established through crystal structure determinations for [(1,3-C₅(Si(CH₃)₃)₂H₃)Ti(CH₃COCHCOCH₃)₂]⁺TfO⁻ and [(1,3-C₅(Si(CH₃)₃)₂H₃)Ti(CF₃COCHCOCF₃)₂OTf].

Cationic transition-metal complexes possessing an available coordination site promote a number of important reactions, including olefin polymerizations,² alkene and alkyne hydrogenations,³ and many others.⁴ The high

reactivity associated with these complexes arises at least in part from the enhanced electrophilicity of the metal center, which favors strong coordination of the organic fragments. However, the extreme Lewis acidity of the cationic site can lead to variety of deactivation processes, including atom abstraction from a reactive solvent⁵ and strong coordination of the solvent required to solubilize an ionic complex.⁶ For these reasons, it would often be desirable to conduct catalytic transformations in solvents of low nucleophilicity and reactivity, such as saturated alkanes or perfluoroalkanes. Unfortunately, cationic transition-metal complexes tend to be rigorously insoluble in such media. We have therefore sought to develop ligands for cationic complexes that boost solubility in nonpolar solvents without kinetically deactivating the resultant species.⁷ In this context, we report the synthesis, structure, and solubility of complexes of the formula [(η⁵-C₅(Si(CH₃)₃)_nH_{5-n})Ti(acac)₂]⁺OTf⁻ (n = 2, 3; acac = CH₃, CF₃, and ^tBu 2,4-disubstituted acetylacetonates). These complexes exhibit modest to excellent solubility in alkane and perfluoroalkane solvents and demonstrate that ionic complexes can be solubilized into even the most nonpolar solvents with the appropriate choice of ligands.

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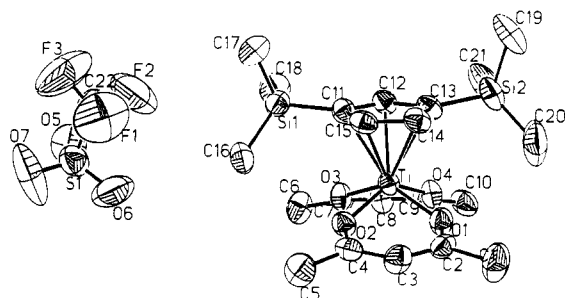


Figure 1. Perspective view of **1**. Selected bond lengths (Å) and angles (deg): Ti–O(1) 1.951 (4), Ti–O(2) 1.958 (4), Ti–O(3) 1.971 (4), Ti–O(4) 1.969 (4), Ti–C(11) 2.379 (5), Ti–C(12) 2.340 (5), Ti–C(13) 2.369 (5), Ti–C(14) 2.357 (5), Ti–C(15) 2.371 (5); O(1)–Ti–O(2) 83.0 (2), O(1)–Ti–O(3) 136.8 (1), O(1)–Ti–O(4) 82.0(2), O(2)–Ti–O(3) 81.4 (2), O(2)–Ti–O(4) 136.5 (1), O(3)–Ti–O(4) 82.2 (2).

Treatment of (1,3-bis(trimethylsilyl)cyclopentadienyl)titanium trichloride^{7b,8a} with silver triflate (1.0 equiv) and acetylacetonate RCOCH₂COR (2 equiv, R = CH₃, ^tBu, CF₃) in refluxing dichloromethane for 4–10 h afforded the triflate complexes [(1,3-C₅(Si(CH₃)₃)₂H₃)Ti(CH₃COCHCOCH₃)₂]⁺TfO⁻ (**1**, 76%), [(1,3-C₅(Si(CH₃)₃)₂H₃)Ti(^tBuCOCHCO^tBu)₂]⁺TfO⁻ (**2**, 71%), and [(1,3-C₅(Si(CH₃)₃)₂H₃)Ti(CF₃COCHCOCF₃)₂OTf] (**3**, 83%; eq 1). Similar reactions using (1,2,4-tris(trimethylsilyl)-

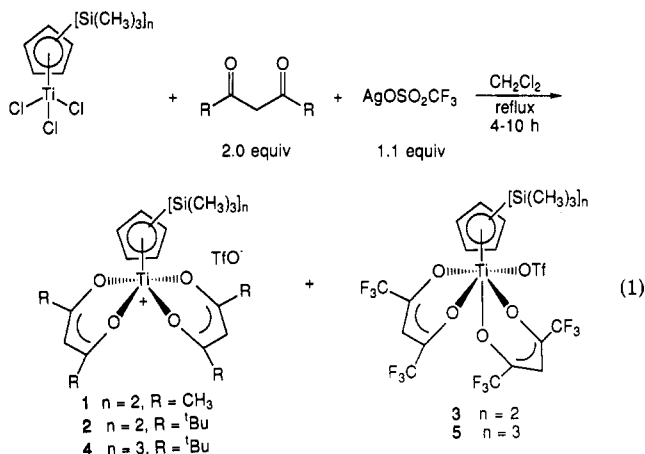


Figure 2. Perspective view of **3**, with acac fluorines omitted for clarity. Selected bond lengths (Å) and angles (deg): Ti–O(1) 2.007 (5), Ti–O(2) 2.168 (5), Ti–O(3) 2.052 (5), Ti–O(4) 2.027 (6), Ti–O(5) 2.018 (5), Ti–C(1) 2.412 (7), Ti–C(2) 2.363 (7), Ti–C(3) 2.357 (7), Ti–C(4) 2.379 (8), Ti–C(5) 2.417 (7); O(1)–Ti–O(2) 79.3 (2), O(1)–Ti–O(3) 152.9 (2), O(1)–Ti–O(4) 93.8 (2), O(1)–Ti–O(5) 88.9 (2), O(2)–Ti–O(3) 73.9 (2), O(2)–Ti–O(4) 74.3 (2), O(2)–Ti–O(5) 77.2 (2), O(3)–Ti–O(4) 82.8 (2), O(3)–Ti–O(5) 81.5 (2), O(4)–Ti–O(5) 150.3 (2).

Table I. Solubilities^a of 1–5 in Cyclohexane and Perfluoromethylcyclohexane

complex	cyclohexane		perfluoromethylcyclohexane	
	M ^b	g/100 mL ^c	M ^b	g/100 mL ^c
1	0.008	0.5	~0.0	~0.0
2	0.020	1.5	0.0004	0.03
3	0.060	4.9	0.0085	0.70
4	0.030	2.5	0.0007	0.06
5	>0.25	>22	0.017	1.5
(1,3-C ₅ (Si(CH ₃) ₃) ₂ H ₃)-TiCl ₃	0.10	3.7	0.017	0.62

^aSolubilities determined as saturated solutions at 23 °C.

^bSolubilities expressed in mol/L. ^cSolubilities expressed in g/100 mL.

pectively, along with selected bond lengths and angles. Complex **1** is ionic in the solid state, with the triflate oxygens being >4 Å from titanium. The cyclopentadienyl ligand is bonded to titanium in a η⁵ fashion, with an average titanium–carbon distance of 2.36 Å. The titanium–acetylacetonate oxygen distances average 1.96 Å. A notable feature is the large empty coordination site that is trans to the cyclopentadienyl ligand. The angle between the planes of the acetylacetonate ligands (defined by Ti, O(1), O(2) and Ti, O(3), O(4)) is 122°, which indicates the size of the open site. Complex **3**, in contrast, is molecular in the solid state and exists in an approximately octahedral geometry. One diketonate ligand spans an axial and equatorial site, while the other is bonded to two equatorial sites. The cyclopentadienyl ligand is bonded in a normal η⁵ fashion, with an average titanium–carbon bond length of 2.38 Å. The three equatorial titanium–oxygen bonds (Ti–O(1), Ti–O(3), Ti–O(4)) range between 2.01 and 2.05 Å, while the axial Ti–O(2) bond length is 2.168 (5) Å. The titanium–triflate oxygen distance is 2.018 (5) Å. The molecular nature of **3** can be rationalized on the basis of the increased Lewis acidity imparted by the trifluoromethyl substituents.

Table I lists the solubilities of complexes **1**–**5** in cyclohexane and perfluoromethylcyclohexane. The ionic complexes **1**, **2**, and **4** exhibit solubilities of 0.008, 0.020, and 0.030 M in cyclohexane, while in the less polar perfluoromethylcyclohexane these values are ~0, 0.0004, and 0.0007 M, respectively. For **4**, these values translate into solubilities of 2.5 g/100 mL in cyclohexane and 0.06 g/100 mL in perfluoromethylcyclohexane. The molecular complexes

cyclopentadienyl)titanium trichloride^{8b} and RCOCH₂COR (R = ^tBu, CF₃) afforded [(1,2,4-C₅(Si(CH₃)₃)₃H₂)Ti(^tBuCOCHCO^tBu)₂]⁺TfO⁻ (**4**, 68%) and [(1,2,4-C₅(Si(CH₃)₃)₃H₂)Ti(CF₃COCHCOCF₃)₂OTf] (**5**, 76%; eq 2). Complexes **1**, **2**, and **4** could be handled in air for several hours without noticeable effect, while **3** and **5** rapidly decomposed upon exposure to ambient atmosphere. Structures were assigned on the basis of ¹H and ¹³C NMR and IR spectroscopy, mass spectrometry, and microanalytical data.⁹

The crystal structures of **1** and **3** were determined to understand the bonding involved in these complexes.¹⁰ Figures 1 and 2 show perspective views of **1** and **3**, re-

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(9) The supplementary material contains full spectral and analytical data for **1**–**5**.

(10) Crystal data for **1**: C₂₂H₃₅F₉O₇SSi₂Ti, monoclinic crystal system, space group P2₁/n, a = 10.612 (3) Å, b = 20.199 (7) Å, c = 14.567 (5) Å, β = 104.27 (5)°, V = 3026 (1) Å³, Z = 4, d_{calc} = 1.327 g/cm³, θ/2θ scanning technique, refined in a full matrix with the programs of SHELX-76, R = 0.055. Crystal data for **3**: C₂₂H₂₃F₁₅O₇SSi₂Ti, monoclinic crystal system, space group P2₁/n, a = 10.512 (3) Å, b = 15.469 (7) Å, c = 21.386 (5) Å, β = 92.55 (2)°, V = 3474 (2) Å³, Z = 4, d_{calc} = 1.569 g/cm³, θ/2θ scanning technique, refined in a full matrix with the programs of SHELX-76, R = 0.078.

3 and **5** are far more soluble than the ionic complexes, as exemplified by their solubilities of 0.060 and >0.25 M in cyclohexane and 0.0085 and 0.017 M in perfluoromethylcyclohexane, respectively. For **5**, this indicates solubilities of >22 g/100 mL in cyclohexane and 1.5 g/100 mL in perfluoromethylcyclohexane. Addition of a third trimethylsilyl group leads to a significant increase in solubility, although the diketone substituents also clearly play a role in solubility enhancement.

To the best of our knowledge, **1**, **2**, and **4** represent the first examples of cationic transition-metal complexes bearing an open coordination site that possess substantial solubilities in alkane and perfluoroalkane solvents. These species are probably tightly ion-paired in these media but still appear to be ionic, since the molecular complexes **3** and **5** exhibit considerably higher solubilities. The results of this study provide a rational basis for increasing the solubility of transition-metal complexes in nonpolar media through the use of polysilylated cyclopentadienes and

substituted acetylacetonates. The fact that the worst case scenario (i.e., cationic complex solubility in cyclohexane and perfluoromethylcyclohexane) is easily achieved implies that simple ligand modification should allow the use of less reactive nonpolar solvents in cases where solvent coordination or reactivity is a problem. The extensive reaction chemistry of **1-5** will be reported in due course.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Supplementary Material Available: Tables listing positional parameters, thermal parameters, complete bond lengths and angles, and full experimental details for data collection and refinement for **1** and **3**, text giving experimental details for the preparation of **1-5**, and tables of spectroscopic and analytical data for **1-5** (25 pages); tables of observed and calculated structure factors for **1** and **3** (48 pages). Ordering information is given on any current masthead page.

Vertical Four-Electron-Donor Alkyne Ligands in (Tris(3,5-dimethylpyrazolyl)borato)niobium Complexes

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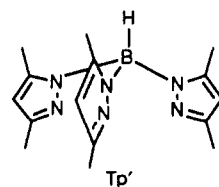
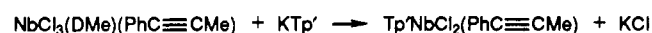
Summary: Reaction of $\text{NbCl}_3(\text{DME})(\text{PhC}\equiv\text{CMe})$ with KTp' in THF produces a high yield of $\text{Tp}'\text{NbCl}_2(\text{PhC}\equiv\text{CMe})$. The solid-state structure of $\text{Tp}'\text{NbCl}_2(\text{PhC}\equiv\text{CMe})$ has the alkyne ligand in the molecular mirror plane, and NMR data are compatible with retention of this alkyne orientation in solution.

Alkyne orientation is an important parameter in alkyne coordination chemistry. This informative probe, which has been particularly well studied in the field of four-electron alkyne ligands,¹ reflects the influence of both electronic and steric interactions.

Consider the geometries found for the extensive family of $\text{Cp}'\text{MX}_2(\text{RC}\equiv\text{CR}')$ complexes ($\text{Cp}' = \eta^5\text{-C}_5\text{H}_5\text{-Me}_x$; $\text{M} = \text{Nb, Ta}$; $\text{X} = \text{halide, alkyl, alkoxy}$; R or $\text{R}' = \text{alkyl, aryl}$). For all but one category of alkyne, namely benzyne ligands, the alkyne has been shown to lie parallel to the cyclopentadienyl ring and perpendicular to the molecular mirror plane in the solid state; spectral data are compatible with retention of this alkyne orientation in solution.^{2,3} An exception was revealed by the X-ray structure of ($\eta^5\text{-C}_5\text{Me}_5$)TaMe₂(C₆H₄),⁴ where benzyne lies in the molecular mirror plane ("vertical"), and the low barrier to rotation, less than 9 kcal mol⁻¹, yields an average NMR signal for the ends of the alkyne even at -80 °C. For the whole series, the barrier to alkyne rotation about the metal-alkyne bond is low (ca. ≤11 kcal mol⁻¹).^{2a} We report here the synthesis and structure of tris(3,5-dimethylpyrazolyl)borate (Tp') derivatives of niobium of the type $\text{Tp}'\text{NbX}_2(\text{PhC}\equiv\text{CMe})$ that exhibit the vertical alkyne orientation as their ground-state geometry.

Reaction of $\text{NbCl}_3(\text{DME})(\text{PhC}\equiv\text{CMe})$ (synthesized according to the method of Hartung and Pedersen⁵) with 1 equiv of KTp' in THF overnight proceeds smoothly to give a red solution from which red crystals of $\text{Tp}'\text{NbCl}_2(\text{PhC}\equiv\text{CMe})$ (**1**) are isolated in 80% yield after workup (eq 1).⁶

Reaction of $\text{NbCl}_3(\text{DME})(\text{PhC}\equiv\text{CMe})$ (synthesized according to the method of Hartung and Pedersen⁵) with 1 equiv of KTp' in THF overnight proceeds smoothly to give a red solution from which red crystals of $\text{Tp}'\text{NbCl}_2(\text{PhC}\equiv\text{CMe})$ (**1**) are isolated in 80% yield after workup (eq 1).⁶



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