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assess the extent and the chemical consequences of such interactions.

Synthesis of [η⁵-(Diphenylphosphino)cyclopentadienyl][η⁷-(diphenylphosphino)cycloheptatrienyl]titanium and Its Utility in the Formation of Heterobimetallic Complexes: The Molecular Structure of Tetracarbonyl{[η⁵-(diphenylphosphino)cyclopentadienyl][η⁷-(diphenylphosphino)cycloheptatrienyl]titanium-*P,P'*}chromium Hemitoluene Solvate

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Treatment of $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)'$Ti with 2.4 equiv of *n*-BuLi/TMEDA followed by reaction with Ph₂PCl has afforded the titanium diphosphine complex $(\eta^5\text{-}C_5H_4PPh_2)(\eta^7\text{-}C_7H_6PPh_2)$Ti (5) in high yield. Complex 5 reacts with a variety of metal carbonyls in refluxing toluene to produce a series of chelated heterobimetallic compounds, including $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^7\text{-}C_7H_6PPh_2)Ti]M(CO)_4$ [M = Cr (6); Mo (7)], $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^7\text{-}C_7H_6PPh_2)Ti](\eta^5\text{-}C_5H_5Co)$ (8), and $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^7\text{-}C_7H_6PPh_2)Ti]Fe(CO)_3$ (9). ³¹P NMR spectra of both 7 and 9 indicate phosphorus–phosphorus coupling as a result of coordination to the same metal atom. The crystal structure of the hemitoluene solvate of 6 has been carried out. It crystallizes in the triclinic space group $P\bar{1}$ with (at -150 °C) a = 10.478 (6) Å, b = 11.012 (7) Å, c = 17.679 (8) Å, α = 82.05 (5)°, β = 79.39 (5)°, γ = 84.01 (5)°, and D_{calcd} = 1.31 g cm⁻³ for Z = 2. A toluene molecule is disordered about a center of inversion. The phosphino groups are both on the same side and coordinated to the Cr atom (Cr–P(average) = 2.43 (2) Å). The Ti–C(η^7) and Ti–C(η^5) distances average 2.19 (1) and 2.31 (2) Å, respectively, with an observed Cent(C₅)–Ti–Cent(C₇) angle of 173.5°. The parent compound 5 was also crystallographically characterized. 5 is monoclinic, $P2_1/c$, with (at 20 °C) a = 8.611 (3) Å, b = 18.633 (5) Å, c = 9.110 (3) Å, β = 98.02 (3)°, and D_{calcd} = 1.31 g cm⁻³ for Z = 2. The molecule is disordered about a crystallographic center of inversion; the phosphorus atoms thus are trans to one another. Important parameters include Ti–C(η^7) = 2.19 (5) Å (average), Ti–C(η^5) = 2.34 (3) Å (average), and Cent(C₅)–Ti–Cent(C₇) = 175.8°.

Introduction

There is currently considerable interest in the synthesis, properties, and structures of heterobimetallic compounds in which the two metals are held in close proximity by heterodifunctional ligands.[3,4] Studies have focused especially on complexes that contain both early (electron-deficient) and middle or late (electron-rich) transition metals, since such systems might exhibit cooperative reactivity.[3,4] While heterobimetallics with a wide variety of bridging ligands are now known, some of the most readily accessible systems are those derived from metallocene-type units that contain two symmetrically positioned diphenylphosphino substituents. These compounds may be regarded as chelating diphosphines that are linked by an organometallic moiety. Subsequent reactions with metal carbonyls or with transition-metal halides lead directly to heterobimetallic compounds in which the two phosphine units become chelated to the second metal. 1,1'-Bis(diphenylphosphino) derivatives of ferrocene,[5–10] cobaltoc-

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(3) Bullock, R. M.; Casey, C. P. *Acc. Chem. Res.* 1987, *20*, 167. See also references cited therein.
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ene,[11] cobaltocenium ion,[7] zirconocene dichloride,[12] and bis(η^6-benzene)chromium[13] have been converted to heterobimetallic compounds in this manner, and the properties and structures of the resulting products have been examined.

Of particular relevance to the present investigation was the report by Tikkanen and co-workers[12] that 1,1'-bis-(diphenylphosphino)zirconocene dichloride (1) reacted

1   2
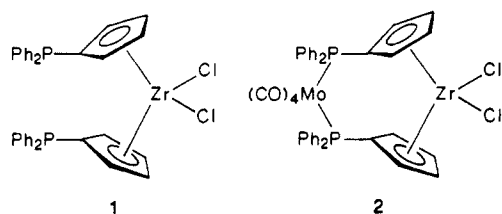
with (η^4-norbornadiene)tetracarbonylmolybdenum to produce tetracarbonyl{bis[(diphenylphosphino)cyclopentadienyl]dichlorozirconium-P,P'}molybdenum (2), whose molecular structure was determined by X-ray diffraction techniques. The structure of 2 was remarkable in that, despite chelation of the molybdenum atom by 1, the coordination spheres of both metals showed only slightly distorted pseudotetrahedral and octahedral geometry, presumably because 1 could undergo rotation of the two canted cyclopentadienyl rings to find the least sterically hindered conformation upon coordination.

In order to further examine the structures and reactivities of heterobimetallic compounds of this general type, we have initiated a study of analogous systems, including (η^5-cyclopentadienyl)(η^7-cycloheptatrienyl)titanium (3).

3   4
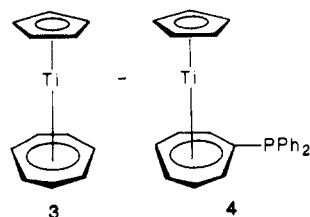
Although 3 has been known since 1970,[14] its reaction chemistry has not been extensively developed. On the other hand, 3 is known to have a *sandwich* structure[15] (uncommon in group 4 organometallic chemistry), is readily synthesized in sizeable quantities,[16,17] and can be metalated by organolithium reagents.[18] Moreover, Dix-

neuf and co-workers have prepared the monophosphine derivative 4 and demonstrated that it was capable of coordinating to other transition metals.[16]

In this paper, we describe the preparation and properties of the new bidentate organometallic compound [η^5-(diphenylphosphino)cyclopentadienyl][η^7-(diphenylphosphino)cycloheptatrienyl]titanium (5) and its reactions

5   6: M = Cr
                     7: M = Mo
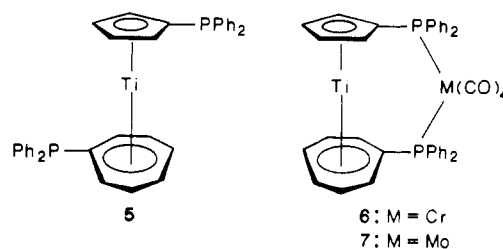
with a variety of metal carbonyls, leading to chelated heterobimetallic compounds. In addition, the molecular structure of one of these products, tetracarbonyl{[η^5-(diphenylphosphino)cyclopentadienyl][η^7-(diphenylphosphino)cycloheptatrienyl]titanium-P,P'}chromium (6) has been elucidated by means of single-crystal X-ray diffraction.

Results and Discussion

An earlier investigation by Groenboom et al. demonstrated that 3 was readily metalated by 1 equiv of n-butyllithium in diethyl ether solution at 0 °C.[18] Following treatment with iodomethane, ^{1}H NMR examination of the reaction mixture indicated that two methylated products were formed, viz., (η^5-C_5H_5)(η^7-$C_7H_6CH_3$)Ti and (η^5-$C_5H_4CH_3$)(η^7-C_7H_7)Ti, in a ratio of 95:5. The metalation of 5 thus takes place preferentially on the seven-membered ring.

Previous studies in our laboratory have shown that ferrocene is readily dimetalated by n-butyllithium–TMEDA (TMEDA = N,N,N',N'-tetramethylethylenediamine) and that the resulting dilithium intermediate could be converted into heteroannularly disubstituted ferrocenes in very high yields.[19,20] It was therefore of interest to examine the possible dimetalation of 3 under these conditions. Accordingly, 3 was added to 2.4 equiv of n-butyllithium–TMEDA in hexane solution at room temperature. A subsequent reaction with chlorodiphenylphosphine followed by crystallization of the product from toluene produced 5 as blue–green crystals in 93% yield.[21] Diphosphine 5 was characterized by elemental analysis, ^{1}H NMR spectroscopy, and a ^{31}P NMR spectrum that exhibited two sharp singlets at δ 17.5 and –18.8 ppm. The mass spectrum of 5 exhibited an intense peak at m/e 572 corresponding to the molecular ion.

The reaction between equimolar amounts of 5 and $Mo(CO)_6$ in refluxing toluene readily afforded the new heterobimetallic compound 7 as light green crystals in 96% yield. The mass spectrum of 7 exhibited a molecular ion at m/e 780 as well as fragmentation peaks resulting from loss of each of the carbonyl substituents. The ^{31}P NMR spectrum of 7 was notable in that both phosphorus reso-

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(21) Groenboom et al.[18] also briefly investigated the possible dimetalation of 3 by n-butyllithium–TMEDA, followed by reaction with iodomethane. Under their conditions, (η^5-$C_5H_4CH_3$)(η^7-$C_7H_6CH_3$)Ti was produced in only relatively low yield and was grossly contaminated by the product resulting from monometalation, (η^5-C_5H_5)(η^7-$C_7H_6CH_3$)Ti.
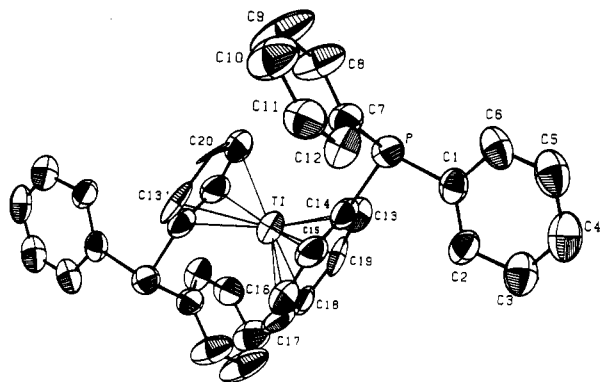
Figure 1. Molecular structure and atom-labeling scheme for **5**. The atoms are represented by their 50% probability ellipsoids for thermal motion. H atoms were not located.

Table I. Bond Distances (Å) and Angles (deg) for $(\eta^5\text{-}C_5H_4PPh_2)(\eta^7\text{-}C_7H_6PPh_2)Ti$

Bond Distances			
Ti–C(13)	2.18 (2)	Ti–C(14)	2.13 (1)
Ti–C(15)	2.24 (1)	Ti–C(16)	2.10 (1)
Ti–C(17)	2.23 (2)	Ti–C(18)	2.22 (2)
Ti–C(19)	2.20 (2)	Ti–C(13)'	2.36 (2)
Ti–C(20)	2.31 (2)	Ti–C(14)[a]	2.34 (1)
Ti–C(15)[a]	2.30 (1)	Ti–C(16)[a]	2.37 (1)
P–C(1)	1.840 (9)	P–C(7)	1.85 (1)
P–C(14)	1.83 (1)	Ti–Cent1[b]	1.45
Ti–Cent2	1.99		
Bond Angles			
C(1)–P–C(7)	100.9 (4)	C(1)–P–C(14)	102.2 (4)
C(7)–P–C(14)	104.2 (5)	Cent1–Ti–Cent2	175.8

[a] Atoms related to those in Table IV by a crystallographic center of inversion. [b] Cent1 is the centroid of the C_7 ring; Cent2 is the centroid of the C_5 ring.

Table II. Bond Distances (Å) and Angles (deg) for $[(\eta^5\text{-}C_5H_4PPh_2)(\eta^7\text{-}C_7H_6PPh_2)Ti]Cr(CO)_4\cdot 0.5C_6H_5Me$

Bond Distances			
Cr–P(1)	2.445 (4)	Cr–P(2)	2.415 (3)
Cr–C(1)	1.88 (1)	Cr–C(2)	1.82 (1)
Cr–C(3)	1.85 (1)	Cr–C(4)	1.89 (1)
Ti–C(29)	2.17 (1)	Ti–C(30)	2.18 (1)
Ti–C(31)	2.19 (1)	Ti–C(32)	2.19 (1)
Ti–C(33)	2.22 (2)	Ti–C(34)	2.20 (2)
Ti–C(35)	2.19 (1)	Ti–C(36)	2.30 (1)
Ti–C(37)	2.32 (1)	Ti–C(38)	2.33 (1)
Ti–C(39)	2.33 (1)	Ti–C(40)	2.29 (1)
Cent1–Ti[a]	1.46	Cent2–Ti	1.98
Bond Angles			
P(1)–Cr–P(2)	99.1 (1)	P(1)–Cr–C(1)	87.6 (4)
P(2)–Cr–C(1)	98.2 (3)	P(1)–Cr–C(2)	171.8 (4)
P(2)–Cr–C(2)	88.8 (4)	C(1)–Cr–C(2)	89.0 (6)
P(1)–Cr–C(3)	87.9 (5)	P(2)–Cr–C(3)	171.0 (4)
C(1)–Cr–C(3)	87.7 (5)	C(2)–Cr–C(3)	84.6 (6)
P(1)–Cr–C(4)	98.5 (4)	P(2)–Cr–C(4)	83.9 (3)
C(1)–Cr–C(4)	173.1 (6)	C(2)–Cr–C(4)	84.5 (6)
C(3)–Cr–C(4)	89.4 (5)	Cent1–Ti–Cent2	173.5

[a] Cent1 is the centroid of the C_7 ring; Cent 2 is the centroid of the C_5 ring.

nances at δ 59.2 and 32.2 ppm were deshielded relative to the resonances for **5** as a result of coordination. Moreover, both resonances appeared as *doublets*, with a J_{P-P} coupling constant of 29 Hz. This strong phosphorus–phosphorus coupling interaction in **7** compared to **5** provides strong evidence that both diphenylphosphino substituents in **7** are coordinated to the same metal atom.

A similar reaction between equimolar amounts of **5** and $Cr(CO)_6$ produced emerald-green crystals of the chromium analogue **6** in 83% yield. Elemental analysis indicated that **6** incorporated 0.5 mol of toluene upon crystallization from that solvent, and this conclusion has been corroborated by results of an X-ray diffraction study (vide infra).

In an analogous manner, reactions of diphosphine **5** with either $(\eta^5\text{-}C_5H_5)Co(CO)_2$ or $Fe_2(CO)_9$ in refluxing toluene gave the new chelated heterobimetallic compounds **8** and **9** in yields of 98% and 38%, respectively. The titanium–
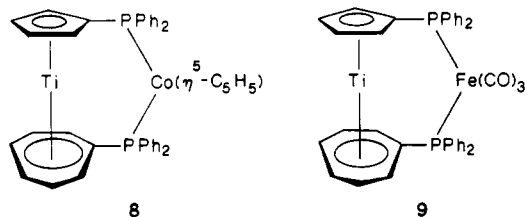
iron product **9**, like **7**, exhibited two deshielded resonances in its ^{31}P NMR spectrum, and both resonances also appeared as doublets with J_{P-P} = 44 Hz. The mass spectrum of **9** contained a molecular ion peak at m/e 712 as well as peaks for losses of each carbonyl substituent. The IR spectrum of **9** showed 3 strong terminal carbonyl frequencies at 1978, 1917, and 1890 cm^{-1}, as would be expected for a cis-chelated diphosphine system containing a $Fe(CO)_3$ moiety.[22]

Diphosphine **5** as well as the heterobimetallic derivatives **6–9** are slightly sensitive in air. However, they can be stored for long periods of time under argon at room temperature. Additional reactions of **5** as well as its dilithium precursor are currently under study in our laboratories.

The molecular structure of **5** is depicted in Figure 1, and important bond distances and angles are given in Table I. The structure of **5** is disordered about a crystallographic center of inversion, and thus only the gross features of the structure can be discussed. The most important aspect of this molecule that can readily be ascertained is the *trans* orientation of the phosphorus atoms. The P–C(14)–C-(14)'–P[a] torsion angle is 180° by symmetry. Despite the disorder the average Ti–C(η^5), Ti–Cent(C_5), Ti–C(η^7), and

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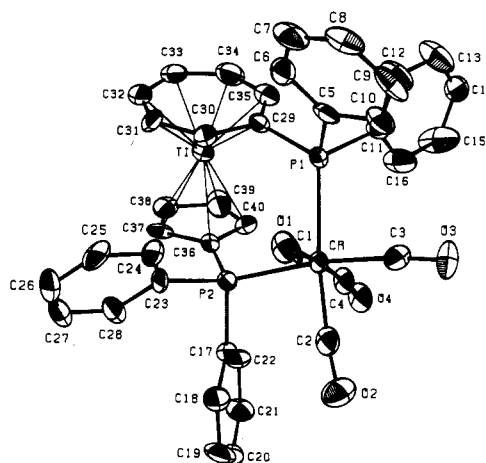**Figure 2.** Molecular structure of **6**. The solvent molecule is not shown.

Ti–Cent(C_7) distances of 2.34 (3), 1.99, 2.19 (5), and 1.45 Å, respectively, are normal. The Cent(C_5)–Ti–Cent(C_7) angle is essentially linear at 175.8°.

In the structure of compound **6**, depicted in Figure 2, the phosphino groups are both on the same side to allow coordination to Cr. The P(1)–C(29)–C(36)–P(2) torsion angle is only 36.0°. From Table II the Cr–P distances differ by 7.5σ, 2.445 (4) Å for Cr–P(1) and 2.415 (3) Å for P(2). The corresponding trans carbonyls are also slightly

different [Cr–C(2) = 1.82 (1) Å, Cr–C(3) = 1.85 (1) Å], the shorter of the two *trans* to the longer Cr–P(1) separation. The remaining two carbonyls are longer with an average Cr–C distance of 1.88 (1) Å. The average Ti–C(η^5), Ti–Cent(C$_5$), Ti–C(η^7), Ti–Cent(C$_7$), and Cent(C$_5$)–Ti–Cent(C$_7$) values are 2.31 (2), 1.98, 2.19 (1), 1.46 Å, and 173.5°, respectively.

An interesting variation in the deviation of the phosphorus atoms from their respective ring planes has been observed. In **5**, the C$_5$ ring is planar to within 0.021 Å and the phosphorus atom deviates out of this plane 0.048 Å away from the Ti center. Similarly, the C$_7$ ring is planar to within 0.032 Å, and again the phosphorus atom deviates away from Ti out of the plane by 0.098 Å. In **6**, however, the bending is different. P(2) bonded to the C$_5$ ring deviates from the plan of this ring 0.09 Å away from the Ti center, while P(1) deviates from the C$_7$ plane toward Ti by 0.19 Å. It is P(1) that exhibits the longer Cr–P approach.

It is fairly evident that the coordination or lack thereof of the attached phosphino groups does not have much of an effect on the bonding of the C$_5$ and C$_7$ rings to the titanium atom. Comparison of the Ti–C(η^5), Ti–Cent(C$_5$), Ti–C(η^7), Ti–Cent(C$_7$), and Cent(C$_5$)–Ti–Cent(C$_7$) parameters for **5**, **6**, (η^5-C$_5$H$_5$)(η^7-C$_7$H$_7$)Ti (**3**),[15] (η^5-C$_5$Me$_5$)(η^7-C$_7$H$_7$)Ti,[23-25] and [(η^5-C$_5$H$_5$)(η^7-C$_7$H$_6$PPh$_2$)Ti]Mo(CO)$_5$·C$_6$H$_5$CH$_3$[16] reveals all of these parameters to be identical within 3σ.

Experimental Section

All operations were carried out under an argon atmosphere by using standard Schlenk or vacuum line techniques, except where specified. Argon was deoxygenated with activated BTS catalyst and dried with molecular sieves and phosphorus pentoxide. Diethyl ether, pentane, and toluene were distilled under argon from sodium–potassium alloy. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA) was obtained from Aldrich Chemical Co. and was dried and distilled from calcium hydride. NMR spectra were recorded on a JEOL FX-90Q, Varian XL-200, or Varian XL-300 spectrometer. IR spectra were recorded on a Perkin-Elmer 1310 spectrometer. Mass spectra were obtained at 70 eV on a Varian CH7 mass spectrometer. Microanalyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA. Melting points were taken in sealed tubes under argon and are uncorrected. (η^5-Cyclopentadienyl)(η^7-cycloheptatrienyl)titanium was prepared by a literature procedure.[16,17] Neutral grade CAMAG alumina was deactivated with degassed water (5%) before use.

[η^5-(Diphenylphosphino)cyclopentadienyl][η^7-(diphenylphosphino)cycloheptatrienyl]titanium (5). Into a 200-mL Schlenk flask were placed 60 mL of pentane, 7.7 mL (12 mmol) of *n*-butyllithium in hexane, and 2.2 mL (15 mmol) of TMEDA. (η^5-Cyclopentadienyl)(η^7-cycloheptatrienyl)titanium (1.0 g, 4.9 mmol) was added over 10 min with stirring. Within minutes, the mixture darkened and gas was evolved. Stirring was continued for 20 h at room temperature, then a room-temperature water bath was attached, and chlorodiphenylphosphine (3.7 g, 17 mmol) was added dropwise via a pipette over a 1-h period. Heat was evolved during the addition, although the mixture warmed only slightly because of the bath. The mixture was stirred for 30 min, and then 10 mL of diethyl ether was added. After additional stirring for 2 h at room temperature, the solvents were removed in vacuo. The residue was extracted with hot toluene and filtered while hot through filter-aid. A deep blue-green

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solution resulted, from which light blue-green crystals formed as the solution was slowly cooled to -20 °C (2.6 g, 93%); mp 90 °C dec. Anal. Calcd for C$_{36}$H$_{30}$P$_2$Ti: C, 75.53; H, 5.28. Found: C, 75.38; H, 5.35. ^{1}H NMR (toluene-d_8): δ 5.09 (m, 2 H, C$_5$H$_4$), 5.22 (m, 2 H, C$_5$H$_4$), 5.45–5.65 (m, 6 H, C$_7$H$_6$), 7.0–7.5 (m, 20 H, Ph). ^{31}P NMR (toluene-d_8, 18 °C): δ -18.8 (s), 17.5 (s). MS: *m/e* 572 (M$^+$).

[(η^5-C$_5$H$_4$PPh$_2$)(η^7-C$_7$H$_6$PPh$_2$)]Mo(CO)$_4$ (7). A solution of (η^5-C$_5$H$_4$PPh$_2$)(η^7-C$_7$H$_6$PPh$_2$)Ti (1.18 g, 2.06 mmol) and Mo(CO)$_6$ (0.54 g, 2.0 mmol) in 75 mL of toluene was allowed to reflux until gas evolution ceased (ca. 1 h). The solution was filtered while hot through filter-aid and was slowly cooled to 0 °C. The supernatant liquid was then decanted from light green crystals of [(η^5-C$_5$H$_4$PPh$_2$)(η^7-C$_7$H$_6$PPh$_2$)]Mo(CO)$_4$. Cooling of the decanted solution to -20 °C afforded a second crop of crystals. The combined crops amounted to 1.5 g (96%); mp 110 °C dec. Anal. Calcd for C$_{40}$H$_{30}$O$_4$P$_2$MoTi: C, 61.54; H, 3.87. Found: C, 61.61; H, 4.10. ^{1}H NMR (CDCl$_3$): δ 5.3–5.6 (m, 10 H, C$_5$H$_4$ and C$_7$H$_6$), 7.1–7.6 (m, 20 H, Ph). ^{31}P NMR (CDCl$_3$): δ 59.2 (d, J_{P-P} = 29 Hz), 32.2 (d, J_{P-P} = 29 Hz). IR (KBr): ν_{CO} 2020 (s), 1865 (br) cm^{-1}. MS: *m/e* 780 (M$^+$), 752 (M – CO)$^+$, 724 (M – 2 CO)$^+$, 696 (M – 3 CO)$^+$, 668 (M – 4 CO)$^+$.

[(η^5-C$_5$H$_4$PPh$_2$)(η^7-C$_7$H$_6$PPh$_2$)Ti]Cr(CO)$_4$ (6). A solution of (η^5-C$_5$H$_4$PPh$_2$)(η^7-C$_7$H$_6$PPh$_2$)Ti (400 mg, 0.7 mmol) in 30 mL of toluene was treated with Cr(CO)$_6$ (150 mg, 0.7 mmol). The reaction mixture was allowed to reflux for 30 h, during which time it became dark green. The solution was then filtered while hot and allowed to cool slowly to room temperature. After 24 h, emerald-green crystals of [(η^5-C$_5$H$_4$PPh$_2$)(η^7-C$_7$H$_6$PPh$_2$)Ti]Cr(CO)$_4$ had formed (430 mg, 83%). The complex incorporates 0.5 mol of toluene/mol of **6** upon crystallization. Anal. Calcd for C$_{40}$H$_{30}$O$_4$P$_2$CrTi·1/2C$_7$H$_8$: C, 66.76; H, 4.38. Found: C, 66.77; H, 4.35. ^{1}H NMR (toluene-d_8): δ 4.9–5.8 (m, 10 H, C$_5$H$_4$ and C$_7$H$_6$), 7.6–8.0 (m, 20 H, Ph). IR (KBr): δ_{CO} 2010 (s), 1870 (br) cm^{-1}.

[(η^5-C$_5$H$_4$PPh$_2$)(η^7-C$_7$H$_6$PPh$_2$)Ti](η^5-C$_5$H$_5$)Co (8). The complexes (η^5-C$_5$H$_4$PPh$_2$)(η^7-C$_7$H$_6$PPh$_2$)Ti (1.00 g, 1.75 mmol) and (η^5-C$_5$H$_5$)Co(CO)$_2$ (0.30 g, 1.7 mmol) were dissolved in 50 mL of toluene and heated under gentle reflux for 20 h. The hot solution was filtered and cooled to room temperature. The solution was concentrated to ca. 20 mL, a layer of pentane was carefully added, and the mixture was cooled to -20 °C. A red solid deposited, from which the supernatant liquid was decanted. The residue was redissolved in toluene and passed through a 5 × 5 cm column of 5% deactivated alumina. The solvent was removed in vacuo, depositing 1.16 g (98%) of [(η^5-C$_5$H$_4$PPh$_2$)(η^7-C$_7$H$_6$PPh$_2$)-Ti](η^5-C$_5$H$_5$)Ti as a red solid. The complex incorporates 0.5 mol of toluene/mol of **8** in crystallization. Anal. Calcd for C$_{41}$H$_{35}$P$_2$CoTi·1/2C$_7$H$_8$: C, 72.36; H, 4.78. Found: C, 72.16; H, 4.71. ^{1}H NMR (C$_6$D$_6$): δ 4.57, 4.63 (m, 4 H, C$_5$H$_4$), 5.11 (s, 5 H, C$_5$H$_5$), 5.52 (m, 6 H, C$_7$H$_6$), 7.12, 7.23 (m, 20 H, C$_6$H$_5$).

[(η^5-C$_5$H$_4$PPh$_2$)(η^7-C$_7$H$_6$PPh$_2$)Ti]Fe(CO)$_3$ (9). A solution of (η^5-C$_5$H$_4$PPh$_2$)(η^7-C$_7$H$_6$PPh$_2$)Ti (0.68 g, 1.19 mmol) and Fe$_2$(CO)$_9$ (0.43 g, 1.18 mmol) in 100 mL of toluene was allowed to reflux for 56 h. The hot solution was filtered, and the solvent was removed in vacuo. The residue was redissolved in a mixture of hexane/toluene, and the solution was chromatographed under argon on alumina. Elution with 1:3 hexane/toluene followed by pure toluene removed a dark green band. The solution was concentrated, a layer of pentane was carefully added, and the mixture was cooled to -20 °C, producing [(η^5-C$_5$H$_4$PPh$_2$)(η^7-C$_7$H$_6$PPh$_2$)Ti]Fe(CO)$_3$ as a green solid. The supernatant liquid was decanted, concentrated, and cooled to afford a second crop of solid. The combined crops weighed 0.32 g (38%). Anal. Calcd for C$_{39}$H$_{30}$O$_3$P$_2$FeTi: C, 65.75; H, 4.24. Found: C, 65.55; H, 4.33. ^{1}H NMR (toluene-d_8):. δ 5.31 (m, 4 H, C$_5$H$_4$), 5.4–5.7 (m, 6 H, C$_7$H$_6$), 7.3–7.8 (m, 20 H, C$_6$H$_5$). ^{31}P NMR (toluene-d_8): δ 62.5 (d, J_{P-P} = 44 Hz), 86.6 (d, J_{P-P} = 44 Hz). IR (toluene): ν_{CO} 1978, 1919, 1890 cm^{-1}. MS: *m/e* 712 (M$^+$), 684 (M – CO)$^+$, 656 (M – 2 CO)$^+$, 628 (M – 3 CO)$^+$, 572 [M – Fe(CO)$_3$]$^+$.

X-ray Data Collection, Structure, Determination, and Refinement for 5 and 6. Compound **5** was mounted in a thin-walled glass capillary, and data were collected at 20 °C. A transparent single crystal of **6** was mounted on a pin and transferred to the goniometer. This crystal was cooled to -150 °C during data collection using a stream of cold nitrogen gas. The space group was **5** was uniquely determined to be *P*2$_1$/*c* from the

Table III. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

	5	6
color/shape	green/parallelepiped	green/parallelepiped
fw	572.5	782.6
space group	$P2_1/c$	$P\bar{1}$
temp, °C	20	−150
cell constants[a]		
a, Å	8.611 (3)	10.478 (6)
b, Å	18.633 (5)	11.012 (7)
c, Å	9.110 (3)	17.679 (8)
α, deg		82.05 (5)
β, deg	98.02 (3)	79.39 (5)
γ, deg		84.01 (5)
cell vol, Å³	1447	1979.2
formula units/unit cell	2	2
D_{calcd}, g cm⁻³	1.31	1.31
μ_{calcd}, cm⁻¹	3.80	5.44
diffractometer/scan	Enraf-Nonius CAD-4/θ-2θ	
radiatn, graphite monochromator	Mo Kα (λ = 0.71073 Å)	
max cryst dimens, mm	0.13 × 0.30 × 0.35	0.10 × 0.33 × 0.33
scan width	0.80 + 0.35 tan θ	0.80 + 0.35 tan θ
std reflctns	400; 060; 004	050; 005; 300
decay of std	±1	±1
reflctns measd	2807	3697
2θ range, deg	2 ≤ 2θ ≤ 50	2 ≤ 2θ ≤ 40
range of h,k,l	+10,+22,±10	+10,±10,±17
reflctns obsd	1206 [$F_o \geq 5\sigma(F_o)$][b]	2802 [$F_o \geq 2.5\sigma(F_o)$][b]
computer programs[c]	SHELX[24]	
struct soln	heavy-atom techniques	
no. of parameters varied	208	445
weights	$[\sigma(F_o)^2 + 0.0006F_o^2]^{-1}$	unit
GOF	2.22	3.37
$R = \sum\lVert F_o\rvert - \lvert F_c\rVert/\sum\lvert F_o\rvert$	0.082	0.077
R_w	0.083	0.093
largest feature final diff map, e Å⁻³	0.4	0.3

[a] Least-squares refinement of $((\sin \theta)/\lambda)^2$ values for 25 reflections, $\theta > 20°$. [b] Corrections: Lorentz–polarization. [c] Neutral scattering factors and anomalous dispersion corrections from ref 25.

Table IV. Final Fractional Coordinates for (η^5-C$_5$H$_4$PPh$_2$)(η^7-C$_7$H$_6$PPh$_2$)Ti

atom	x/a	y/b	z/c	B(eq),[a] Å²
Ti	0.4578 (4)	0.4927 (3)	0.4962 (7)	2.95
P	0.3705 (3)	0.6385 (1)	0.2224 (3)	3.11
C(1)	0.270 (1)	0.6267 (6)	0.032 (1)	2.98
C(2)	0.193 (1)	0.5628 (5)	−0.012 (1)	3.27
C(3)	0.106 (1)	0.5586 (6)	−0.158 (1)	4.11
C(4)	0.105 (1)	0.6174 (7)	−0.251 (1)	4.26
C(5)	0.187 (1)	0.6792 (6)	−0.206 (1)	4.37
C(6)	0.265 (1)	0.6856 (6)	−0.064 (1)	3.87
C(7)	0.573 (1)	0.6560 (5)	0.187 (1)	3.14
C(8)	0.656 (1)	0.7068 (6)	0.280 (1)	5.34
C(9)	0.811 (2)	0.7204 (8)	0.259 (2)	7.46
C(10)	0.881 (1)	0.6869 (7)	0.149 (2)	5.68
C(11)	0.793 (1)	0.6380 (6)	0.053 (1)	4.13
C(12)	0.637 (1)	0.6240 (6)	0.075 (1)	3.66
C(13)[b]	0.241 (2)	0.547 (1)	0.407 (2)	3.43
C(13)'	0.718 (2)	0.482 (1)	0.617 (2)	3.96
C(14)	0.377 (1)	0.5468 (5)	0.294 (1)	3.32
C(15)	0.473 (1)	0.4908 (6)	0.252 (1)	3.70
C(16)	0.459 (1)	0.4235 (6)	0.314 (1)	4.50
C(17)	0.382 (3)	0.386 (1)	0.401 (2)	3.90
C(18)	0.261 (2)	0.414 (1)	0.474 (2)	3.27
C(19)	0.201 (2)	0.484 (1)	0.473 (2)	3.68
C(20)	0.677 (3)	0.559 (1)	0.589 (3)	5.35

[a] $B(\text{eq}) = \frac{4}{3}[a^2\beta(11) + b^2\beta(22) + c^2\beta(33) + ab(\cos \gamma)\beta(12) + ac(\cos \beta)\beta(13) + bc(\cos \alpha)\beta(23)]$. [b] Atoms C(13), C(13)', and C(17)–C(20) have occupancy factors of 0.5.

Table V. Final Fractional Coordinates for [(η^5-C$_5$H$_4$PPh$_2$)(η^7-C$_7$H$_6$PPh$_2$)Ti]Cr(CO)$_4$•0.5C$_6$H$_5$Me

atom	x/a	y/b	z/c	B(eq),[a] Å²
Cr	0.0313 (2)	0.1291 (2)	0.2266 (1)	1.51
Ti	0.4549 (2)	0.2468 (2)	0.2036 (1)	2.08
P(1)	0.1094 (3)	0.2813 (3)	0.2919 (2)	1.59
P(2)	0.2209 (3)	0.0982 (3)	0.1283 (2)	1.45
O(1)	−0.1214 (8)	0.3334 (7)	0.1395 (4)	2.07
O(2)	−0.1128 (9)	−0.0434 (8)	0.1630 (5)	3.17
O(3)	−0.2094 (8)	0.1182 (8)	0.3462 (5)	2.93
O(4)	0.1353 (9)	−0.1094 (7)	0.3095 (4)	2.65
C(1)	−0.056 (1)	0.261 (1)	0.1715 (6)	1.48
C(2)	−0.050 (1)	0.023 (1)	0.1849 (7)	2.26
C(3)	−0.115 (1)	0.126 (1)	0.3029 (8)	1.93
C(4)	0.103 (1)	−0.015 (1)	0.2799 (6)	1.91
C(5)	0.007 (1)	0.427 (1)	0.2892 (6)	1.87
C(6)	0.051 (1)	0.541 (1)	0.2541 (7)	2.52
C(7)	−0.034 (2)	0.646 (1)	0.2526 (8)	3.08
C(8)	−0.162 (2)	0.645 (1)	0.2860 (8)	2.78
C(9)	−0.206 (1)	0.535 (1)	0.3226 (7)	2.82
C(10)	−0.125 (1)	0.426 (1)	0.3235 (7)	2.56
C(11)	0.105 (1)	0.245 (1)	0.3969 (6)	1.73
C(12)	0.087 (1)	0.336 (1)	0.4444 (7)	3.33
C(13)	0.090 (2)	0.309 (2)	0.5225 (8)	4.18
C(14)	0.111 (2)	0.190 (2)	0.5544 (7)	3.91
C(15)	0.127 (2)	0.099 (1)	0.5084 (8)	5.47
C(16)	0.122 (2)	0.126 (1)	0.4295 (7)	3.93
C(17)	0.224 (1)	−0.0539 (9)	0.0961 (6)	1.26
C(18)	0.149 (1)	−0.072 (1)	0.0443 (7)	2.66
C(19)	0.143 (1)	−0.189 (1)	0.0231 (7)	3.06
C(20)	0.218 (1)	−0.286 (1)	0.0540 (7)	2.75
C(21)	0.299 (1)	−0.272 (1)	0.1054 (7)	2.66
C(22)	0.302 (1)	−0.155 (1)	0.1272 (7)	2.25
C(23)	0.240 (1)	0.194 (1)	0.0339 (6)	2.04
C(24)	0.172 (1)	0.307 (1)	0.0239 (7)	2.00
C(25)	0.183 (1)	0.379 (1)	−0.0501 (8)	2.97
C(26)	0.265 (2)	0.335 (1)	−0.1121 (8)	3.58
C(27)	0.334 (2)	0.222 (1)	−0.1025 (7)	3.30
C(28)	0.324 (1)	0.150 (1)	−0.0299 (7)	2.97
C(29)	0.274 (1)	0.334 (1)	0.2606 (6)	1.68
C(30)	0.295 (1)	0.378 (1)	0.1764 (7)	2.37
C(31)	0.413 (1)	0.418 (1)	0.1302 (8)	2.54
C(32)	0.534 (2)	0.421 (1)	0.1495 (8)	2.91
C(33)	0.574 (2)	0.392 (1)	0.2220 (9)	3.40
C(34)	0.496 (1)	0.347 (1)	0.2948 (8)	3.29
C(35)	0.362 (1)	0.324 (1)	0.3099 (8)	2.65
C(36)	0.378 (1)	0.0913 (9)	0.1543 (6)	1.63
C(37)	0.498 (1)	0.119 (1)	0.1069 (7)	1.82
C(38)	0.598 (1)	0.095 (1)	0.1473 (8)	2.81
C(39)	0.545 (2)	0.046 (1)	0.2258 (8)	2.93
C(40)	0.411 (1)	0.044 (1)	0.2292 (7)	2.00
C(41)	0.5852	0.1877	0.5535	(iso)
C(42)	0.6810	0.2453	0.5266	(iso)
C(43)	0.7385	0.3243	0.5631	(iso)
C(44)	0.6767	0.3591	0.6346	(iso)
C(45)	0.5572	0.3148	0.6697	(iso)
C(46)	0.4997	0.2358	0.6332	(iso)
C(47)	0.5418	0.1375	0.5340	(iso)
C(48)	0.4688	0.2302	0.5275	(iso)
C(49)	0.4405	0.3559	0.5076	(iso)
C(50)	0.5287	0.4392	0.5138	(iso)
C(51)	0.6451	0.3966	0.5398	(iso)
C(52)	0.6733	0.2709	0.5597	(iso)

[a] $B(\text{eq}) = \frac{4}{3}[a^2\beta(11) + b^2\beta(22) + c^2\beta(33) + ab(\cos \gamma)\beta(12) + ac(\cos \beta)\beta(13) + bc(\cos \alpha)\beta(23)]$.

systematic absences. 6 was found to be either $P\bar{1}$ or $P1$. Statistical tests indicated that the space group was centric and the subsequent solution and successful refinement of the structure in the space group $P\bar{1}$ confirmed this. A summary of data collection parameters is given in Table III.

It was immediately obvious in the solution of 5 that the structure was disordered about a center of inversion. The disorder is such that the PPh$_2$ groups [P, C(1)–C(6), C(7)–C(12)] are in fact ordered and only the C$_5$ and C$_7$ rings are disordered. C(14), C(15), and C(16) are common to both rings and are full weighted. C(13) and C(17)–C(19) complete the C$_7$ ring and are half weighted. C(13)' and C(20) complete the C$_5$ ring and are also half weighted.

The difference in Ti–C(η^7) and Ti–C(η^5) separations results in the Ti atom also fractionally disordered about the center of inversion. As a result, the Ti–C(η^7) distances are shorter as expected. Due to the proximity of the disordered carbon atoms, refinement of the rings was very poor. No hydrogen atoms were included. Final position parameters for **5** are given in Table IV.

Several diffuse peaks near a center of inversion were observed in a difference Fourier map for **6**. Analysis of these positions revealed a toluene molecule in four different positions (two related by the center of inversion). One position [C(41)] was common to both unique orientations and was given an occupancy of 0.5. Another position [C(50)] corresponded to an aryl carbon atom on one side of the inversion center and a methyl group on the other side and was also given an occupancy of 0.5. The remaining ten carbon atoms were given occupancies of 0.25. Due to the proximity of the carbon atom positions, the refinement was poor. In the final cycles, each group of six ring atoms was idealized and only the isotropic thermal parameters were allowed to refine. The hydrogen atoms (except for those associated with the toluene molecule) were included in calculated positions 0.95 Å from the

bonded carbon atom and allowed to ride on that atom with *B* fixed at 5.5 Å². Final positional parameters for **6** are given in Table V.

Supplementary Material Available: Full tables of bond distances and angles, H atom coordinates, thermal parameters, and least-squares results (11 pages); listings of structure factors (9 pages). Ordering information is given on any current masthead page.

Protonation of Nickel–Molybdenum and Nickel–Tungsten Alkyne Complexes with Trifluoroacetic Acid Affording μ-η¹,η²-Alkenyl Species: X-ray Structure of NiW(CO)₂(μ-η¹,η²-(*E*)-C(Me)=CHMe)(η⁵-C₅H₅)(η⁵-C₅H₄Me)-(CO₂CF₃)

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Protonation of the heterodinuclear bridging alkyne complexes NiM(CO)₂(μ-η²,η²-RC₂R′)(η⁵-C₅H₅)(η⁵-C₅H₄Me) (M = Mo, RC₂R′ = MeC₂Me; M = W, RC₂R′ = HC₂H, MeC₂Me, *n*-PrC₂H, PhC₂H) with trifluoroacetic acid affords the neutral alkenyl complexes NiM(CO)₂(μ-η¹,η²-(*E*)-CR=CHR′)(η⁵-C₅H₅)(η⁵-C₅H₄Me)(CO₂CF₃), in which the alkenyl ligand is σ-bonded to the group 6 metal and π-bonded to the nickel atom. In some cases, the alkenyl complexes are in equilibrium with the alkyne species: the position of the equilibrium depends on the particular complex and on the solvent. Proton addition is regio- and stereospecific: isomers obtained result from Markovnikov addition to the alkyne. The nickel–tungsten isomer containing the alkenyl ligand μ-η¹,η²-C(Ph)=CH₂, resulting from Markovnikov addition, can be thermally isomerized to the anti-Markovnikov isomer NiW(CO)₂(μ-η¹,η²-(*E*)-CH=CHPh)(η⁵-C₅H₅)(η⁵-C₅H₄Me)(CO₂CF₃). Deuteration of the nickel–tungsten ethyne, 1-pentyne, or phenylacetylene complexes with trifluoroacetic acid-*d*₁, afforded (*Z*)-alkenyl-*d*₁ species. However, the 2-butenylnickel–molybdenum complex exists as an equilibrium mixture of *E* and *Z* isomers, and the complex NiW(CO)₂(μ-η¹,η²-(*Z*)-C-(Ph)=CHD)(η⁵-C₅H₅)(η⁵-C₅H₄Me)(CO₂CF₃) eventually afforded a mixture of *Z* and *E* isomers when allowed to stand in solution. The complexes have been characterized by ¹H and ¹³C NMR and IR spectroscopy and elemental analysis. An X-ray diffraction study was carried out on **2a**, NiW(CO)₂(μ-η¹,η²-(*E*)-C-(Me)=CHMe)(η⁵-C₅H₅)(η⁵-C₅H₄Me)(CO₂CF₃). Crystals of **2a** (C₁₉H₁₉F₃NiO₄W) belong to the monoclinic space group *P2₁/n* (No. 14) with *a* = 8.3710 (7) Å, *b* = 27.609 (5) Å, *c* = 9.045 (1) Å, *β* = 109.210 (7)°, and *Z* = 4.

Introduction

We have been investigating the chemistry of the group 6–group 10 cyclopentadienyl–carbonyl complexes NiM-(CO)₄(η⁵-C₅H₅)(η⁵-C₅H₄Me) with reactive hydrocarbon ligands. The mixed-metal species react with alkynes affording the bridging alkyne complexes NiM(CO)₂(μ-η²,η²-RC₂R′)(η⁵-C₅H₅)(η⁵-C₅H₄Me) (M = Mo, W).[1]

Mechanistic details of these reactions have been reported.[2] The protonation of these alkyne complexes was of interest in order to establish whether this would be a viable route to mixed-metal alkenyl complexes.

Protonation of homodinuclear bridging alkyne complexes to afford μ-η¹,η²-alkenyl species has been observed for dimolybdenum complexes,[3,4] and an uncommon in-

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