metals[7,18] and to other ligands are currently in progress.

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Registry No. **1a**, 82661-46-9; **1b**, 92144-96-2; **1c**, 92144-97-3; **2**, 92144-98-4; **3a**, 92144-99-5; **3b**, 75687-68-2; **4a**, 92145-01-2; **4b**, 92145-03-4; **4c**, 92145-05-6; **5**, 92145-06-7.

Supplementary Material Available: Tables of atomic coordinates and temperature factors, bond lengths, bond angles, anisotropic temperature factors, hydrogen coordinates, and temperature factors (Tables I-V) and observed and calculated structure factors (Table VI) (32 pages). Ordering information is given on any current masthead page.

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Reactions of Coordinated Molecules. 41. Addition of a Pt–H Bond across a M≡C Bond: A Direct Route to a Heterodinuclear μ-Alkylidene Complex

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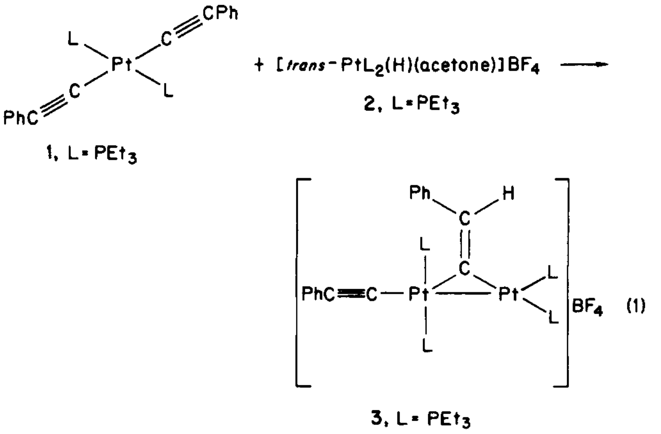
Summary: When the alkylidyne complex $(\eta\text{-}C_5H_5)(OC)_2W{\equiv}C\text{-}C_6H_4CH_3\text{-}p$ is treated with $[trans\text{-}Pt(PEt_3)_2(H)(acetone)]BF_4$, the μ-alkylidene complex $\{(\eta\text{-}C_5H_5)(OC)_2W[\mu\text{-}\eta^1,\eta^3\text{-}C(C_6H_4CH_3\text{-}p)(H)]Pt(PEt_3)_2\}BF_4$ is formed. This reaction demonstrates the conversion of a terminal carbyne ligand to a μ-alkylidene complex with concomitant formation of a heterodinuclear cluster.

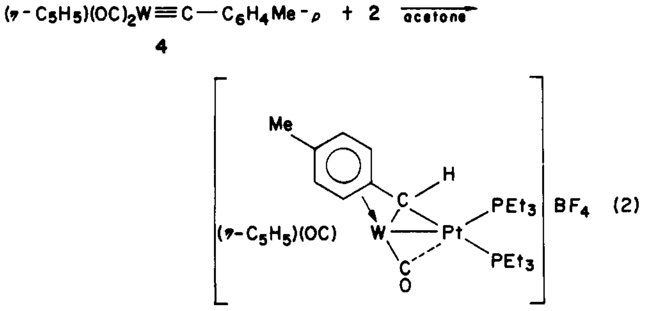
We reported recently that the Pt–H bond of the cationic metal hydride complex $[trans\text{-}Pt(PEt_3)_2(H)(acetone)]BF_4$, **2**, adds across the C–C triple bond of the neutral phenyl acetylide complex $trans\text{-}Pt(PEt_3)_2(C{\equiv}CPh)_2$, **1**, to give the cationic dinuclear cluster **3** that contains a μ-phenylvinylidene ligand (eq 1).[1]



The formation of **3** by this route represents a new type of bridge-assisted, addition reaction for cluster synthesis.[2] This reaction parallels the well-studied addition of **2** (and related complexes) to the C–C triple bonds of alkynes.[3] The Pt–H bond polarity of **2** is presumably $^{\delta-}Pt\text{–}H^{\delta+}$,[3a] so the addition of **2** to **1** occurs with the expected regioselectivity of having the electrophilic hydrogen atom attack C_β of the phenyl acetylide ligand.[4] This mode of addition converts the terminal phenyl acetylide ligand into a μ-phenylvinylidene ligand.

The possibility of adding reagents like **2** to other types of unsaturated bonds as a general method for preparing homo- and heterodinuclear clusters is under investigation. We now wish to report that the Pt–H bond of **2** adds across the M–C triple bond of a terminal alkylidyne ligand to form a heterodinuclear cluster which has a μ-alkylidene ligand.

When a solution of 0.175 g (0.43 mmol) of the neutral, terminal alkylidyne complex $(\eta\text{-}C_5H_5)(OC)_2W{\equiv}C\text{-}C_6H_4CH_3\text{-}p$, **4**,[5] in 5 mL of acetone is added to an acetone solution of **2** (0.43 mmol)[6] and the reaction solution is stirred for an additional 1 h at 25 °C, the heterodinuclear cluster **5** is formed (eq 2). Complex **5** is isolated as amber crystals by crystallization from a 5:1 THF/pentane solution at −20 °C.[7] The assigned molecular structure of **5** is supported by microanalytical data and the nearly identical agreement of the IR and ^{1}H NMR data between **5** and the structurally characterized PMe_3 analogue to **5** that has been reported by Stone et al.[8] However, an X-ray structural determination of **5** is anticipated to confirm the structure shown and to provide another example of a $\mu\text{-}\eta^1,\eta^3\text{-}C(C_6H_4CH_3\text{-}p)(R)$ ligand type.[8,9] Complex **5** is



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[7] Detailed characterization data for complex **5** are as follows: yield 0.18 g, 45%; mp 145–148 °C dec; IR(CH_2Cl_2) ν(CO) 1960 (vs), 1810 (br, m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.03 (m, 18, CH_3, J_{HH} = 4 Hz, J_{PH} = 8 Hz), 1.94 (m, 12, CH_2, J_{HH} = 4 Hz, J_{PH} = 8 Hz), 2.32 (s, 3, aryl CH_3), 4.76 (s, 5, C_5H_5), 5.94 (d, 1, C_6H_4, J_{HH} = 6 Hz), 6.74 (d, 1, μ-CH, J_{PH} = 7 Hz), 7.00, 7.20, 7.41 (m, 3, C_6H_4). Anal. Calcd for $C_{27}H_{40}BF_4O_2P_2PtW$: C, 34.97; H, 4.67. Found: C, 34.83; H, 4.70.

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formed directly from **4** and **2** whereas the PMe_3 analogue to **5** was prepared by Stone et al. in a two-step process by reacting **4** with a source of $Pt(PMe_3)_2{}^0$ followed by protonation of the isolated μ-alkylidyne cluster with $HBF_4 \cdot Et_2O$.[8]

The results of eq 1 and 2 indicate that **2** (and possibly related complexes) might be *generally* useful reagents for preparing clusters from compounds containing unsaturated bonds at appropriate locations by either *formal* insertion or proton transfer reactions. These reactions complement the recent extensive cluster chemistry of Stone[10] with the important difference that in this method *the "addition" of the Pt–H bond to the reactant complex changes the identity of the eventual bridging ligand.* A study of the reactions of **2** (and related species) with other alkylidyne complexes and other compounds containing unsaturated bonds is being pursued.

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Registry No. 2, 84623-75-6; 4, 60260-15-3; 5, 92145-08-9; Pt, 7440-06-4; W, 7440-33-7.

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Stereoselective Additions to the Alkoxycarbene Cations $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)({=}CROMe)]^+$ (R = H, Et)

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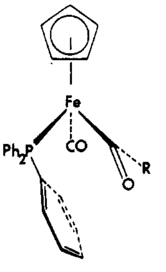
Summary: Nucleophilic addition reactions to the cations $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)({=}CROMe)]^+$ (R = H, Et) are highly stereoselective. The product diastereoisomers $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(CHEtOMe)]$ undergo epimerization in methanol prior to formation of $(E)\text{-}[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(CH{=}CHMe)]$.

We have recently presented a series of guidelines concerning the reactivity of ligands bound to the $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)$ moiety.[1] In particular, it was predicted, by analogy with the acyl complexes **1**, that the alkoxycarbene cations **2** should exist in the anti (O–O) conformation and that high stereoselectivities should be seen in their reactions with nucleophiles.

Several reports of the hydride reductions of cations **2** have appeared with little stereoselectivity apparently being observed.[2,3] More surprising was the reported observation that borohydride in the presence of methoxide smoothly reduced **3** without deprotonation to the corresponding methoxyvinyl complexes[3] especially since we have recently found that this deprotonation is extremely facile.[4] We report here a reexamination of the reduction of complex **3** together with a more extensive description of its reactivity and reduction products.



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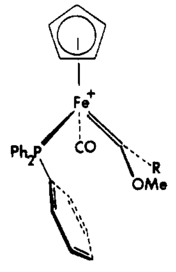
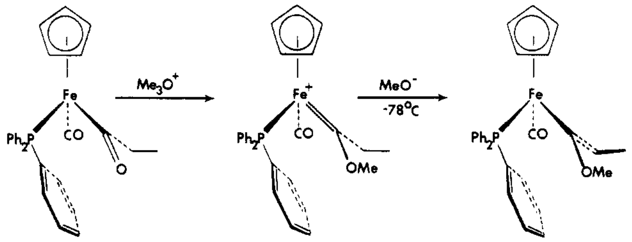


2

Treatment of the acyl complex **4** with trimethyloxonium tetrafluoroborate generated cation **3**.[5] An X-ray crystallographic analysis of **3**[6] showed that as expected[1] the oxygens were anti and one face of the alkoxycarbene ligand was shielded by the proximate phenyl group of the triphenylphosphine ligand. Treatment of **3** with sodium methoxide quantitatively generated the methoxyvinyl complex **5** (*E*:*Z* = 1:100).



4 3 5

In our hands reduction of cation **3** with a variety of hydride reagents (e.g., $LiAlH_4$, $NaBH_4$) in tetrahydrofuran is very stereoselective with the two diastereoisomers **6** and **7** being produced in the ratio 15:1 ($NaBH_4$, −100 °C). The ratio of **6**:**7** dropped to 12:1 when this reduction was performed at −78 °C. The major diastereoisomer is assigned as **6** on the assumption that hydride adds to the unhindered face of the carbene **3** in the anti (O–O) conformation.[1] Diastereoisomer **6** could be isolated pure by crystallization.[7] With use of the literature procedure[3] of adding a dichloromethane solution of **3** to $NaBH_4/NaOMe$ in methanol, a mixture of the reduced products **6** and **7** together with the deprotonated product **5** was obtained in the ratio 8.5:1:4.5, respectively (lit.[3] **6**:**7** = 3:1). Hindered

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[7] 300-MHz ^1H NMR (C_6D_6): **5**, δ 7.7–6.95 (15 H, m, aryl H), 5.30 (1 H, dq, J_{PH} = 5.2 Hz, J_{HH} = 6.3 Hz, vinylic H), 4.36 (5 H, d, J_{PH} = 0.9 Hz, C_5H_5), 2.94 (3 H, s, OCH_3), 2.24 (3 H, d, J_{HH} = 6.4 Hz, CH_3); **6**, 7.6–7.0 (15 H, m, aryl H), 4.40 (5 H, d, J_{PH} = 1.0 Hz, C_5H_5), 4.02 (1 H, ddd, J = 10, 3, 1 Hz, FeCH), 3.46 (3 H, s, OCH_3), 2.3 and 2.0 (2 H, m, m, CH_2), 0.91 (3 H, t, J = 7.5 Hz, CH_3); **7**, 7.7–7.0 (15 H, m, aryl H), 4.39 (5 H, d, J_{PH} = 1.0 Hz, C_5H_5), 3.90 (1 H, ddd, J = 4.6, 8.2, 10 Hz, FeCH), 2.92 (3 H, s, OCH_3), 2.35 and 1.92 (2 H, m, m, CH_2), 1.20 (3 H, t, J = 7.5 Hz, CH_3); **11**, 7.6–7.0 (15 H, m, aryl H), 6.90 (1 H, ddq, J = 6.7, 15.2, 1.4 Hz), 5.74 (1 H, ddq, J = 2.5, 15.2, 5.9 Hz), 4.19 (5 H, d, J = 1.0 Hz, C_5H_5), 2.02 (3 H, ddd, J = 5.9, 1.4, 1.4 Hz, CH_3). 62.90-MHz ^{13}C NMR (C_6D_6): **5**, δ 222.7 (d, J_{PC} = 33.5 Hz, CO), 177.5 (d, J_{PC} = 24 Hz, Fe–C), 103.57 (=CH), 84.63 (C_5H_5), 55.05 (OCH_3), 17.13 (CH_3); **6**, 223.9 (d, J_{PC} = 33.4 Hz, CO), 89.7 (d, J_{PC} = 16.6 Hz, Fe–C), 85.6 (C_5H_5), 58.90 (OCH_3), 41.05 (CH_2), 15.64 (CH_3); **7**, 222.7 (d, J_{PC} = 33 Hz, CO), 89.82 (d, J_{PC} = 19 Hz, Fe–C), 85.77 (C_5H_5), 59.34 (OCH_3), 36.47 (CH_2), 14.56 (CH_3); 11, 222.6 (d, J_{PC} = 31.3 Hz, CO), 138.3 (d, J_{PC} = 29.9 Hz, Fe–C), 137.8 (=C), 84.8 (C_5H_5), 25.4 (CH_3). Anal. Calcd for $C_{28}H_{29}FeO_2P$ (**6**): C, 69.43; H, 6.04; P, 6.39. Found: C, 69.41; H, 6.06; P, 6.64.

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