(Me)=O, 87367-49-5; *t*-BuN=C(H)C(Me,*t*-Bu)OH, 60294-86-2.

Supplementary Material Available: An ORTEP drawing of **1a** and tables of positional and thermal parameters for all atoms and bond lengths and bond angles of $[EtZn(Et)(t\text{-}Bu)NC(H)=C(Me)O]_2$ (**1a**), elemental analyses of the compounds **1a–h** and **2a–e**, and cryoscopic molecular weight determinations of various organozinc compounds in benzene (6 pages); a listing of observed and calculated structure factors for **1a** (8 pages). Ordering information is given on any current masthead page.

Reactions of Coordinated Molecules. 50. The Preparation of Homo- and Heterodinuclear Complexes Containing μ-Alkenylidene Ligands

Dawood Afzal and Charles M. Lukehart*

Department of Chemistry, Vanderbilt University, Nashville, Tennessee

Received May 6, 1986

The formal addition of the Pt–H bond of the cationic complex $[trans\text{-}Pt(H)(PEt_3)_2(acetone)]^+$ across the C–C triple bonds of alkynyl ligands affords cationic dinuclear complexes containing bridging alkenylidene ligands. The synthesis and characterization of eight such complexes are reported. On the basis of structural data for a member complex, these molecules are believed to possess Pt–Pt, Pt–Fe, Pt–Au, Pt–W, Pt–Ni, or Pt–Pd bonds. Diagnostic spectroscopic characterization data are provided. Furthermore, a similar addition of a Pt–Me bond across an acetylide ligand also affords a dinuclear μ-alkenylidene complex.

Introduction

Cluster complexes containing hydrocarbyl fragments as bridging ligands remain of current interest to chemists because of their potential to exhibit new chemistry and their possible structural relationship to surface-bound species. Transition-metal complexes containing μ-alkenylidene ligands are one type of such compounds.[1] Recent reports demonstrate interesting chemistry at μ-alkenylidene ligands,[2] and other studies have confirmed the existence of surface-bound alkenylidene species on Pt and Pd.[3]

Bridging alkenylidene complexes have been prepared by a variety of methods (though some of these have only limited generality) such as alkyne isomerization,[4] halide displacement from *gem*-dihaloalkenes,[5] deprotonation of a μ-alkylidyne ligand,[6] metal coordination to a terminal alkenylidene ligand,[7] oxygen extrusion from diphenylketene,[8] formal dehydrogenation of ethylene,[9] nucleophilic addition to an unsaturated M–alkylidyne ligand[6e] or a $\mu\text{-}\eta^2$-acetylide ligand,[10] elimination of an alcohol from a μ-alkoxyalkylidene ligand[11] or water from μ-hydroxyalkylidene[12] and μ_3-hydroxyethylidyne[13] ligands, thermal degradation of a diruthenacyclopentenone complex,[3c,14] and the use of *N*-nitrosourethanes as a source of alkenylidene fragments.[15] The majority of these μ-alkenylidene com-

(1) Recent review: Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 60–128.

(2) (a) Casey, C. P.; Marder, S. R. *Organometallics* **1985**, *4*, 411–413. (b) Hoel, E. L.; Ansell, G. B.; Leta, S. *Organometallics* **1984**, *3*, 1633–1637. (c) Jacobsen, E. N.; Bergman, R. G. *Organometallics* **1984**, *3*, 329–331. (d) Brum, P.; Dawkins, G. M.; Green, M.; Mills, R. M.; Salaun, J.-Y.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 966–968.

(3) (a) Ibach, H.; Lehwald, S. *J. Vac. Sci. Technol.* **1978**, *15*, 407–415. (b) DeMuth, J. E. *Surf. Sci.* **1979**, *80*, 367–387. (c) Kesmodel, L. L.; Gates, J. A. *J. Electron. Spectrosc. Relat. Phenom.* **1983**, *29*, 307–312. (d) Koestner, R. J.; Frost, J. C.; Stair, P. C.; Van Hove, M. A.; Somorjai, G. A. *Surf. Sci.* **1982**, *116*, 85–103.

(4) (a) Nesmeyanov, A. N.; Aleksandrov, G. G.; Antonova, A. B.; Anisinov, K. N.; Struchkov, Yu. T. *J. Organomet. Chem.* **1976**, *110*, C36–C38. (b) Antonova, A. B.; Kolobova, N. E.; Petrovsky, P. V.; Lokshin, B. V.; Obzyuk, N. S. *Ibid.* **1977**, *137*, 55–67. (c) Kolobova, N. E.; Antonova, A. B.; Khitrova, O. M.; Antipin, M. Yu.; Struchkov, Yu. *T. Ibid.* **1977**, *137*, 55–67. (d) Folting, K.; Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1979**, *18*, 3483–3486. (e) Boland-Lussier, B. E.; Churchill, M. R.; Hughes, R. P.; Rheingold, A. L. *Organometallics* **1982**, *1*, 628–634. (f) Al-Obaidi, Y. N.; Green, M.; White, N. D.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 319–326. (g) Berry, D. H.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 7181–7183.

(5) (a) King, R. B.; Saran, M. S. *J. Am. Chem. Soc.* **1972**, *94*, 1784–1785. (b) King, R. B.; Saran, M. S. *Ibid.* **1973**, *95*, 1811–1817. (c) King, R. B.; Saran, M. S. *Ibid.* **1973**, *95*, 1817–1824. (d) Stang, P. J. *Chem. Rev.* **1978**, *78*, 383–405. (e) Jacobsen, E. N.; Bergman, R. G. *Organometallics* **1984**, *3*, 329–331.

(6) (a) Cooke, M.; Davies, D. L.; Guerchais, J. E.; Knox, S. A. R.; Mead, K. A.; Roue, J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 862–864. (b) Kao, S. C.; Lu, P. P. Y.; Pettit, R. *Organometallics* **1982**, *1*, 911–918. (c) Colburn, R. E.; Davies, D. L.; Dyke, A. F.; Endesfelder, A.; Knox, S. A. R.; Orpen, A. G.; Plaas, D. *J. Chem. Soc., Dalton Trans.* **1983**, 2661–2668. (d) Casey, C. P.; Meszaros, M. W.; Marder, S. R.; Fagan, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 3680–3681. (e) Casey, C. P.; Marder, S. R. *Organometallics* **1985**, *4*, 411–413. (f) Casey, C. P.; Marder, S. R.; Adams, B. R. *J. Am. Chem. Soc.* **1985**, *107*, 7700–7705. (g) Casey, C. P.; Gohdes, M. A.; Meszaros, M. W. *Organometallics* **1986**, *5*, 196–199.

(7) (a) Kolobova, N. E.; Antonova, A. B.; Khitrova, O. M. *J. Organomet. Chem.* **1978**, *146*, C17–C18. (b) Kolobova, N. E.; Ivanov, L. L.; Zhvanko, O. S.; Aleksandrov, G. G.; Struchkov, Yu. T. *Ibid.* **1982**, *228*, 265–272. (c) Antonova, A. B.; Kovalenko, S. V.; Korniyets, E. D.; Petrovsky, P. V.; Gulbis, G. R.; Johansson, A. A. *Inorg. Chim. Acta* **1985**, *916*, 1–7.

(8) Mills, O. S.; Redhouse, A. D. *J. Chem. Soc., Chem. Commun.* **1966**, 444–445.

(9) (a) Deeming, A. J.; Underhill, M. *J. Chem. Soc., Dalton* Trans. **1974**, 1415–1419. (b) Deeming, A. J.; Hasso, S.; Underhill, M.; Canty, A. J.; Johnson, B. F. G.; Jackson, W. G.; Lewis, J.; Matheson, T. W. *J. Chem. Soc., Chem. Commun.* **1974**, 807–808.

(10) Mott, G. N.; Carty, A. J. *Inorg. Chem.* **1983**, *22*, 2726–2736.

(11) Awang, M. R.; Jeffrey, J. C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 2091–2098.

(12) (a) Dawkins, G. M.; Green, M.; Jeffery, J. C.; Stone, F. G. A. *J. chem. Soc., Chem. Commun.* **1980**, 1120–1122. (b) Dawkins, G. M.; Green, M.; Jeffery, J. C.; Sambale, C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 499–506.

(13) Seyferth, D.; Williams, G. H.; Eschbach, C. S.; Nesthe, M. O.; Merola, J. S.; Hallgren, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 4867–4878.

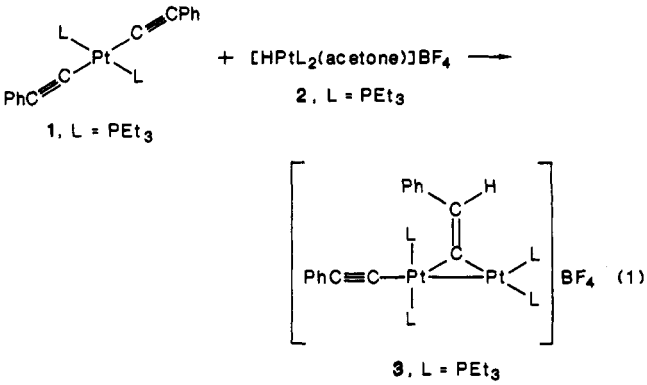
(14) Davies, D. L.; Dyke, A. F.; Endesfelder, A.; Knox, S. A. R.; Naish, P. J.; Orpen, A. G.; Plass, D.; Taylor, G. E. *J. Organomet. Chem.* **1980**, *198*, C43–C49.

(15) Herrmann, W. A.; Ziegler, M. L.; Serhadli, O. *J. Organomet. Chem.* **1985**, *297*, 245–254.

0276-7333/87/2306-0546$01.50/0

plexes contain homonuclear metal cores. To our knowledge, only four heterodinuclear μ-alkenylidene compounds have been prepared.[7,11] These complexes contain Pt–W, Pt–Mn, Mn–Fe, and Mn–Re bonds.

We recently communicated a new method of preparing bridging alkenylidene complexes by the addition of a Pt–H bond across the C–C triple bond of a phenyl acetylide ligand.[16] As shown in eq 1, the Pt–H bond of the cationic



hydride complex **2** adds across one of C–C triple bonds of a phenyl acetylide ligand in **1** with the appropriate regiochemistry to give the cationic diplatinum μ-phenylvinylidene complex **3**. The X-ray structure of **3** confirms the unusual coordination geometries about both formally Pt(I) atoms and a Pt–Pt distance of 2.750 (2) Å.[16] Complex **3** is the first diplatinum μ-alkenylidene complex to be reported, and it serves as a model for μ-alkenylidene coordination to Pt metal surfaces.

We now report (1) more detailed spectroscopic characterization data for complex **3**, (2) the addition of **2** to other alkynyl ligands to give eight μ-alkenylidene complexes containing Pt–Pt, Pt–Fe, Pt–Au, Pt–W, Pt–Ni, or Pt–Pd bonds, and (3) the addition of a Pt–Me bond across an acetylide ligand to afford an analogous μ-alkenylidene complex.

Results and Discussion

The identification of a definitive spectroscopic method for characterizing μ-phenylalkenylidene complexes like **3** is necessary to obviate the need for X-ray crystallographic analysis of each such compound. Attempts to obtain ^{195}Pt NMR spectra of **3** were unsuccessful due to high-field effects, and, although the ^{31}P NMR spectrum of **3** appears to be consistent with the expected AA'BCXY pattern, confirmation of these spectral assignments must await computer simulation due to the low symmetry of **3** and its existence as four magnetically different species.

Fortunately, the 400-MHz ^{1}H NMR spectra of **3** provide a diagnostic indication of the formation of the μ-phenylalkenylidene ligand. When the reaction shown in eq 1 is followed by ^{1}H NMR in acetone solution at 20 °C and at 0.07 M, the product cluster **3** is formed in essentially quantitative yield after 8 min of mixing the reagents. Subsequent spectra taken over 4 days reveal a nearly complete (>96%) conversion of this initial product to another isomer. The aromatic portion of the NMR spectrum recorded after 120 min of reaction is shown in Figure 1 to provide spectral assignments. The doublet at δ 7.92 and the doublet of doublets at δ 7.73 ($^4J_{PH}$ = 21.5 and 9.9 Hz) belong to the kinetically controlled product **3a** while the doublet at δ 8.07 and the doublet of doublets at δ 6.97 ($^4J_{PH}$ = 13.8 and 9.4 Hz) belong to the thermodynamically

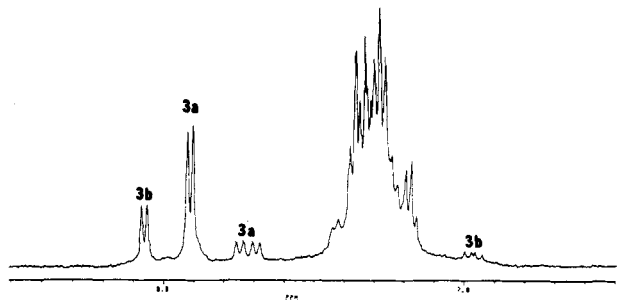
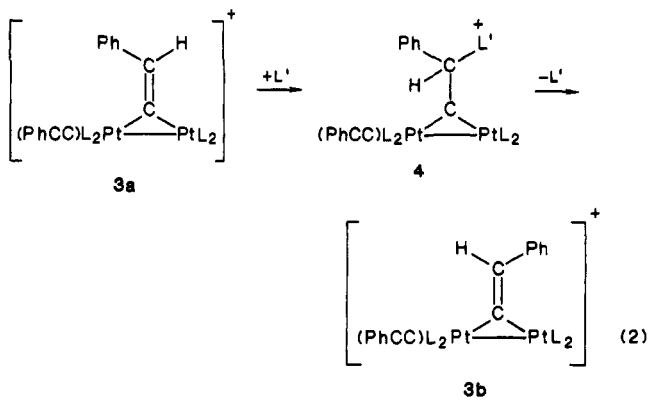


Figure 1. A 400-MHz ^{1}H NMR spectrum in the aromatic/vinylidene region of the reaction solution prepared as shown in eq 1 after 120 min showing the isomer assignments depicted in eq 2. The spectrum is recorded in acetone-d_6 at 20 °C.

controlled product **3b**. The single doublet resonances are assigned to the two ortho protons of the phenyl ring of the μ-phenylalkenylidene ligand, and the doublet of doublets are assigned to the unique alkenylidene proton showing coupling to the two phosphorus nuclei of the formally four-coordinate Pt atom (vide post). The resonances denoted as **3a** are observed also in samples prepared from both bulk single crystals and from the actual data crystal used to determine the X-ray structure of **3**.[16] When the Pt–D analogue to **2** is used in the reaction, the ^{2}H NMR spectrum reveals a deuterium alkenylidene resonance at δ 7.63 (in CD_2Cl_2 solution), thereby confirming the assignment of the unique alkenylidene proton resonance of **3a**.

A proposed mechanism for this isomerization is shown in eq 2. The alkenylidene C–C distance in **3a** of 1.33 (3)

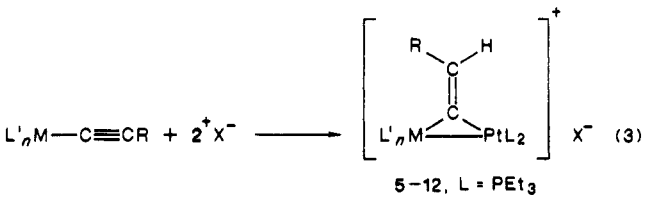


Å represents a normal C–C double bond distance, so relatively facile isomerization about this bond is not expected. In fact, sample solutions prepared from crystalline **3a** do not undergo this isomerization in acetone solution. Presumably, the reaction solution contains a nucleophilic species (perhaps dissociated PEt_3) that catalyzes this isomerization through a benzylic intermediate, such as **4**. Reversible 1,2-addition and β-hydrogen elimination of the Pt–H fragment from **3a** as a possible isomerization mechanism would not explain the apparent inability of **3a** to convert directly to **3b**. When a sample of pure **3a** in acetone solution is treated with a large excess of PEt_3, the solution color changes from orange to yellow and the ortho and alkenylidene proton resonances disappear. A new multiplet resonance appears at δ 3.98. The same experiment with the deuterium alkenylidene analogue to **3a** shows ^{2}H resonances both at δ 3.98 and in the normal aromatic region. These spectral data might support the formation of benzylic species similar to **4**, although complete spectroscopic characterization of this in situ species is not possible. The observed conversion of **3a** to **3b** under the reaction conditions stated above occurs with a first-

(16) Afzal, D.; Lenhert, P. G.; Lukehart, C. M. *J. Am. Chem. Soc.* **1984**, *106*, 3050–3052.

order rate constant of 4.47×10^{-3} min^{-1} and a half-life of 155 min.

The Pt–H bond of **2** adds across the C–C triple bonds of several other alkynyl ligands, as shown in eq 3, to give



compd	L′$_n$M	R	X$^-$
5	L_2(MeC≡C)Pt	Me	PF_6^-
6	L_2(HC≡C)Pt	H	PF_6^-
7	(η-C_5H_5)(μ-CO)(OC)Fe	Ph	PF_6^-
8	$(Ph_3P)Au$	Ph	BF_4^-
9	(η-C_5H_5)$(OC)_3W$	Ph	PF_6^-
10	L_2(PhC≡C)Ni	Ph	PF_6^-
11	L_2(PhC≡C)Pd	Ph	PF_6^-
12	LAu	Ph	PF_6^-

dinuclear clusters containing μ-alkenylidene ligands and presumably Pt–Pt, **5** and **6**, Pt–Fe, **7**, Pt–Au, **8** and **12**, Pt–W, **9**, Pt–Ni, **10**, and Pt–Pd, **11**, bonds. Complexes **5–8** are prepared in 31–73% yield and are isolated as dry solids that can be characterized by microanalysis. Initial microanalytical values for carbon were consistently low due presumably to low combustion temperatures. Reanalysis with tin powder as a combustion additive gave satisfactory values. The primary diagnostic characterization data for these clusters are the observed unambiguous proton or deuterium NMR resonances for the unique alkenylidene protons. Complexes **9–12** could not be isolated as pure dry solids, and complexes **10** and **11** decompose in solution during prolonged attempts at crystallization, so these complexes have been characterized spectroscopically.

The diplatinum complexes **5** and **6** are directly analoguous to **3**. Complex **5** contains a μ-methylalkenylidene ligand and gives a vinylidene proton resonance as a broad multiplet centered at δ 6.25. Complex **6** contains an *unsubstituted* μ-alkenylidene ligand and shows a highly coupled proton resonance centered at δ 5.78. Neither complex contains aromatic substituents that might complicate the assignment of the μ-alkenylidene proton resonances.

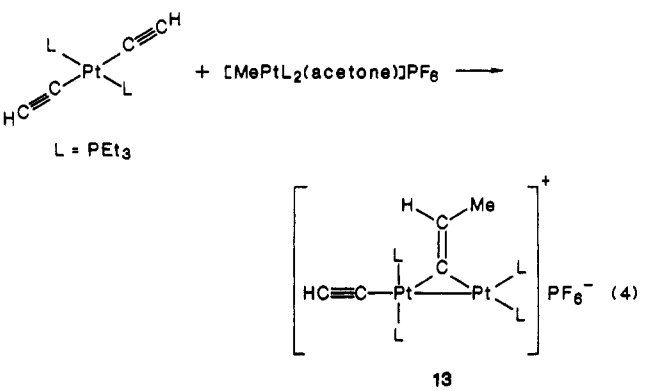
The Pt–Fe complex **7** exhibits carbonyl stretching bands at 2030 and 1880 cm^{-1}, indicating terminal and doubly bridging carbonyl ligands. The unique vinylidene proton resonance of the μ-phenylalkenylidene ligand appears as a doublet of doublets at δ 8.32 ($^4J_{PH}$ = 11.0 and 6.0 Hz, $^3J_{PtH}$ = 20 Hz). Because complex **3** shows a very similar coupling pattern between the PtL_2 moiety and the unique vinylidene proton, we believe that the PtL_2(C≡CPh) moiety of **3** does not couple appreciably to the vinylidene proton. Furthermore, the chemical shift of the unique vinylidene proton of **7** is most consistent with that of the kinetically controlled isomer **3a**, thereby indicating a similar structure for complex **7**. The assignment of the unique vinylidene proton resonance of **7** is confirmed by using the Pt–D derivative of **2**. The corresponding ^{2}H resonance for the vinylidene deuterium appears at δ 8.44 in acetone solution. For the closest known analogue (η-C_5H_5)(μ-CO)(OC)Mn[μ-C=C(Ph)(H)]Pt[$P(OEt_3)_3$]$_2$, the unique vinylidene proton resonance appears at δ 8.76 as a doublet of doublets ($^4J_{PH}$ = 12.5, 12.5 Hz, $^3J_{PtH}$ = 25.6 Hz).[7c]

The Pt–Au complexes **8** and **12** are formed readily, but compound **12** is difficult to purify. Complex **8** contains four phenyl substituents, and its aromatic proton resonances mask the unique vinylidene proton resonance. However, with use of the Pt–D derivative of **2** the ^{2}H NMR spectrum of **8** reveals a resonance at δ 7.98, thereby confirming the presence of a μ-phenylalkenylidene ligand. Complex **12**, which has only one aromatic substituent, shows a unique vinylidene proton resonanace at δ 7.88 as an overlapping set of doublet of doublets ($^4J_{PH}$ = 6.5 Hz).

The Pt–W complex **9** exhibits terminal carbonyl stretching bands at 2150 and 2050 cm^{-1}. A doublet of doublets is observed in the ^{1}H NMR spectrum at δ 8.38 ($^4J_{PH}$ = 5.9 and 1.8 Hz) for the unique vinylidene proton resonance. This chemical shift value might also indicate that **9** is formed as the μ-phenylalkenylidene isomer **3a**. A related Pt–W μ-vinylidene complex, [$(OC)_5$W(μ-C=CH_2)Pt(dppm)], exhibits a similar vinylidene proton resonance at δ 4.01 with P–H coupling of 9 and 11 Hz.[11]

As mentioned above, the Pt–Ni, **10**, and Pt–Pd, **11**, complexes are unstable for prolonged periods in solution. Spectral NMR data of **10** reveal a doublet of doublets centered at δ 7.73 ($^4J_{PH}$ = 9.4 and 4.7 Hz) for the proton resonance of the unique vinylidene proton and a ^{2}H resonance at δ 8.04 (in acetone solution) for the corresponding vinylidene deuterium resonance. Complex **11** has a vinylidene proton resonance at δ 7.88 ($^4J_{PH}$ = 8.0 Hz) and a corresponding vinylidene ^{2}H NMR deuterium resonance at δ 8.05 (in acetone solution). Complex **10** shows a doublet at δ 7.50 of very low intensity that might correspond to the resonance of the ortho phenyl protons of the other isomer of the μ-phenylalkenylidene ligand, as discussed above for **3**.

The reaction shown in eq 4 demonstrates the formation



of a diplatinum μ-methylalkenylidene complex by the addition of a Pt–Me bond across the C–C triple bond of an acetylide ligand. Complex **13** is isolated as a red powder in 30% yield. An acetylide C≡C stretching band is observed at 2080 cm^{-1}. Complex **13** is a very close analogue to compound **5** and differs only in having a terminal acetylide ligand rather than a terminal methyl acetylide ligand. The ^{1}H NMR spectrum of **13** is free of any aromatic absorptions and reveals a complex multiplet of resonances at δ 5.68 and 6.29 for the unique vinylidene proton. The resonance at δ 5.68 has the greater relative intensity. Because complexes **5** and **13** should form opposite μ-methylalkenylidene ligands as the kinetically controlled products of syn Pt–H and Pt–Me additions, respectively, we assign the δ 6.25 isomer of **5** to a structure similar to **3a** and the δ 5.68 isomer of **13** to a structure similar to **3b**. Both of these isomer assignments correspond to the expected kinetically controlled addition products. A kinetic study of the possible methylalkenylidene isomerization of complex **13** in the reaction medium was not performed.

Conclusions

Detailed ^{1}H and ^{2}H NMR spectral characterization of the previously reported diplatinum cluster **3** provides a

diagnostic spectral method for identifying μ-alkenylidene ligands in this class of molecule. Eight new homo- or heterodinuclear complexes containing μ-alkenylidene ligands have been prepared by Pt—H addition across C≡C bonds of alkynyl ligands. In addition, a Pt—Me bond has been shown to insert across a C≡C of an acetylide ligand to give an analogous dinuclear compound. We believe that such addition reactions on coordinated molecules may be a convenient route to cluster complexes containing bridging hydrocarbyl ligands.

Experimental Section

All manipulations were performed under dry, prepurified nitrogen. Solvents were dried using standard methods and were distilled under nitrogen before us.[17] ^{1}H NMR spectra were recorded on a Bruker AM-400 spectrometer operating at a frequency of 400 MHz and at 20 °C and a JEOL FX90Q spectrometer operating at a frequency of 90 MHz and 36 °C, using the ^{2}H signal of the solvent ($CDCl_3$), acetone-d_6, or CD_2Cl_2 as an internal lock frequency. Chemical shifts were measured with respect to internal standard Me_4Si in δ. ^{2}H NMR spectra were recorded on a Bruker AM400 spectrometer at a frequency of 61 MHz. These spectra were recorded in either CH_2Cl_2 or acetone solution by recording the ^{2}H signal from the concentrated deuterium-labeled sample through the lock receiver channel while the sweep was turned off. This signal was Fourier transformed like a regular FID to give the desired spectra. Depending on the sample concentration, ^{2}H spectra were obtained after 200–3500 scans. Chemical shifts were measured by using the residual deuterium signal of the solvent as a standard. Microanalysis was performed by Galbraith Laboratories, Inc., Knoxville, TN, and by MicAnal Microanalysis, Tucson, AZ.

The starting material *trans*-L_2PtHCl was prepared by Parshall's method;[18] and the following metal acetylides **14–22** were prepared by literature methods: *trans*-$L_2Pt(C{\equiv}CR)_2$ (**14** and **15** (R = H or Me));[19] (η-C_5H_5)$(OC)_2Fe(C{\equiv}CPh)$ (**16**);[20] $LAu(C{\equiv}CPh)$ (**17** and **18** (L = PEt_3 or PPh_3));[21,22] (η-C_5H_5)$(OC)_3W(C{\equiv}CPh)$ (**19**);[23] *trans*-$L_2Ni(C{\equiv}CPh)_2$ (**20**);[24] and *trans*-$L_2Pd(C{\equiv}CPh)_2$ (**21**).[25]

Preparation of [Pt_2(μ-C═CHMe)(C≡CMe)(PEt_3)$_4$]PF_6 (5). To a filtered solution of 0.59 mmol of **2**, prepared from 0.28 g of *trans*-$(PEt_3)_2PtHCl$ and 1 equiv of $AgPF_6$ in 50 mL of acetone, was added 0.33 g (a 10% molar excess) of **15** as a solid. The reaction solution was stirred at 25 °C for 44 h. the solvent was removed at reduced pressure, and the obtained orange residue was washed with 3 × 10 mL of diethyl ether to give after drying in vacuo 0.46 g (73%) of **5** as an orange powder: decomp pt 140–145 °C; IR (CH_2Cl_2) ν(C≡C) 2160 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.07–1.25 (m, 36, CH_2CH_3), 1.85–2.13 (m, 30, CH_2CH_3 + CMe + CH*Me*), 6.15–6.35 (m, 1, *CH*Me). Anal. Calcd for $C_{30}H_{67}F_6P_5Pt_2$: C, 33.16; H, 6.16. Found: C, 32.96; H, 6.42.

Preparation of [Pt_2(μ-C═CH_2)(C≡CH)(PEt_3)$_4$]PF_6 (6). To a filtered solution of 0.54 mmol of **2**, prepared from 0.26 g of *trans*-$(PEt_3)_2PtHCl$ and 1 equiv of $AgPF_6$ in 40 mL of acetone, was added 0.20 g (0.54 mmol) of **14** as a solid. The reaction solution was stirred at 25 °C for 4 h. The solvent was removed at reduced pressure, and the resulting orange residue was washed with several portions of diethyl ether to give after drying in vacuo 0.39 g (68%) of **6** as an orange powder: decomp pt 88–90 °C; IR (CH_2Cl_2) ν(C≡C) 2070 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.91–1.34 (m, 36, CH_2CH_3), 1.80–2.25 (m, 25, CH_2CH_3 + CH), 5.38–6.17 (m, 2, μ-C═CH_2). Anal. Calcd for $C_{28}H_{63}F_6P_5Pt_2$: C, 31.78; H, 5.95. Found: C, 31.75; H, 5.97.

Preparation of [FePt(μ-C═CHPh)(C_5H_5)(CO)(μ-CO)(PEt_3)$_2$]PF_6 (7). To a filtered solution of 0.85 mmol of **2**, prepared from 0.41 g of *trans*-$(PEt_3)_2PtHCl$ and 1 equiv of $AgPF_6$ in 50 mL of acetone, was added 0.75 g (0.88 mmol) of **16** as a solid. The reaction solution was stirred at 25 °C for 5 h. The solvent was removed at reduced pressure, and the obtained amber residue was washed with ether/hexane solution to achieve solidification. This solid was crystallized from THF/pentane at −15 °C to afford 0.48 g (62%) of **7** as an orange-red powder: decomp pt 160–165 °C; IR (CH_2Cl_2) ν(CO) 2030 (s), 1880 (m) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 0.83–1.32 (m, 18, CH_2CH_3), 1.86–2.40 (m, 12, CH_2CH_3), 4.97 (s, 5, C_5H_5), 7.20–7.55 (m, 5, Ph), 8.32 (dd, 1, *CH*Ph, $^4J_{PH}$ = 11.0 and 6.0 Hz, $^3J_{PtH}$ = 20 Hz). Anal. Calcd for $C_{26}H_{41}F_6FeP_3Pt$: C, 37.88; H, 4.80; F, 13.33; P, 10.86. Found: C, 38.04; H, 4.65; F, 12.92; P, 10.72.

CDPh analogue to 7: ^{2}H NMR (CH_2Cl_2) δ 8.44 (s, CDPh).

Preparation of [AuPt(μ-C═CHPh)(PPh_3)(PEt_3)$_2$]BF_4 (8). To a filtered solution of 0.94 mmol of **2**, prepared from 0.44 g of *trans*-$(PEt_3)_2$ PtHCl and 1 equiv of $AgBF_4$ in 30 mL of acetone, was added 0.55 g (a 5% molar excess) of **18** as a solid. The reaction solution was stirred at 25 °C for 2 h. The solvent was removed at reduced pressure, and the resulting orange residue was washed with ether/hexane solution to achieve solidification. This solid was crystallized from THF/pentane at −15 °C to give 0.56 g (55%) of **8** as an amber powder: decomp pt 75–80 °C; ^{1}H NMR ($CDCl_3$) δ 1.10–1.30 (m, 18, CH_2CH_3), 2.10–2.36 (m, 12, CH_2CH_3), 6.68–7.97 (m, 21, PPh_3 + Ph + *CH*Ph). Anal. Calcd for $C_{28}H_{51}AuBF_4P_3Pt$: C, 42.29; H, 4.73; P, 8.61. Found C, 41.96; H, 4.75; P, 8.48.

CDPh analogue to 8: ^{2}H NMR (acetone) δ 7.98 (s, CDPh).

Preparation of [PtW(μ-C═CHPh)(CO)$_3$(C_5H_5)(PEt_3)$_2$] PF_6 (9). To a filtered solution of 0.15 mmol of **2**, prepared from 0.07 g of *trans*-$(PEt_3)_2PtHCl$ and 1 equiv of $AgPF_6$ in 15 mL of acetone, was added 0.06 g of **19** as a solid. The reaction solution was stirred at 25 °C for $2^1/_2$ h. The solvent was removed at reduced pressure, and the reaction residue was washed with ether/hexane solution to give a brown, semisolid product: IR (CH_2Cl_2) ν(CO) 2150 (s), 2050 (vs) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90–1.34 (m, 18, CH_2CH_3), 1.95–2.40 (m, 12, CH_2CH_3), 6.37 (s, 5, C_5H_5), 7.20–7.80 (m, 5, Ph), 8.38 ("dd", 1, *CH*Ph, $^4J_{PH}$ = 5.9 and 1.8 Hz).

Preparation of [NiPt(μ-C═CHPh)(C≡CPh)(PEt_3)$_4$]PF_6 (10). To a filtered solution of 0.32 mmol of **2**, prepared from 0.15 g of *trans*-$(PEt_3)_2PtHCl$ and 1 equiv of $AgPF_6$ in 20 mL of acetone, was added 0.17 g of **20** as a solid. The reaction solution was stirred at 25 °C for 2 h. The solvent was removed at reduced pressure, and the brown residue was extracted with THF. The extract was filtered and the product was precipitated as a brown oil upon addition of hexane: ^{1}H NMR (CD_2Cl_2) δ 0.90–1.30 (m, 36, CH_2CH_3), 1.90–2.20 (m, 24, CH_2CH_3), 7.15–7.45 and 7.61 (m, 10, 2Ph), 7.73 (dd, 1, *CH*Ph, $^4J_{PH}$ = 9.4 and 4.7 Hz).

CDPh analogue to 10: ^{2}H NMR (acetone) δ 8.04 (s, CDPh).

Preparation of [PdPt(μ-C═CHPh)(C≡CPh)(PEt_3)$_4$]PF_6 (11). To a filtered solution of 0.39 mmol of **2**, prepared from 0.18 g of *trans*-$(PEt_3)_2PtHCl$ and 1 equiv of $AgPF_6$ in 30 mL of acetone, was added 0.21 g (0.39 mmol) of **21** as a solid. The reaction solution was stirred for 17 h at 25 °C. The solvent was removed at reduced pressure, and the brown reaction residue was washed with 10 mL of diethyl ether to give 0.16 g (36%) of **11** as a brown powder: ^{1}H NMR (acetone-d_6) δ 1.10–1.40 (m, 36, CH_2CH_3), 2.10–2.35 (m, 24, CH_2CH_3), 7.07–7.70 (m, 10, 2Ph), 7.88 ("t", 1, CHPh, $^4J_{PH}$ = 8.0 Hz).

CDPh analogue to 11: ^{2}H NMR(acetone) δ 8.05 (s, CDPh).

Preparation of [AuPt(μ-C═CHPh)(PEt_3)$_3$]PF_6 (12). To a filtered solution of 0.39 mmol of **2**, prepared from 0.18 g of *trans*-$(PEt_3)_2$ PtHCl and 1 equiv of $AgPF_6$ in 30 mL of acetone, was added 0.16 g of **17** as a solid. The reaction solution was stirred for 12 h at 25 °C. The solvent was removed at reduced pressure, and the resulting brown oil was washed with ether to achieve solidification. Compound **12** was isolated as a deep brown powder (0.15 g, 39%): ^{1}H NMR (acetone-d_6) δ 1.37–1.40 (m, 27, CH_2CH_3), 2.00–2.25 (m, 18, CH_2CH_3), 7.15–7.75 (m, 5, Ph), 7.88 ("t", *CH*Ph, $^4J_{PH}$ = 6.5 Hz).

Addition of a Pt–Me Bond across a Pt–Acetylide C–C Triple Bond. Pt_2(μ-C═CHMe)(PEt_3)$_4$(C≡CH)]PF_6 (13). The

(17) Lenhert, P. G.; Lukehart, C. M.; Sacksteder, L. A. *J. Am. Chem. Soc.* **1986**, *108*, 793–800.
(18) Parshall, G. W. *Inorg. Synth.* **1970**, *12*, 27–29.
(19) Sonogashira, K.; Fujikura, Y.; Yatake, T.; Toyoshima, N.; Takahashi, S.; Hagihara, n. *J. Organomet. Chem.* **1978**, *145*, 101–108.
(20) Green, M. L. H.; Mole, T. *J. Organomet. Chem.* **1968**, *12*, 404–406.
(21) Cross, R. J.; Davidson, M. F.; Mclennon, A. J. *J. Organomet. Chem.* **1984**, *265*, C37–39.
(22) Bruce, M. I.; Horn, E.; Matisons, J. G.; Snow, M. R. *Aust. J. Chem.* **1984**, *37*, 1163–1170.
(23) Bruce, M. I.; Humphrey, M. G.; Matisons, J. G.; Roy, S. K.; Swincer, A. G. *Aust. J. Chem.* **1984**, *37*, 1955–1961.
(24) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1960**, 1718–1729.
(25) Sonogashihira, K.; Yatake, T.; Tohda, Y.; Takahashi, S.; Hagihara, N. *J. Chem. Soc., Chem. Commun.* **1977**, 291–292.
(26) Clark, H. C.; Fiess, P. L.; Wong, C. S. *Can. J. Chem.* **1977**, *55*, 177–188.

starting materials *trans*-$L_2Pt(C{\equiv}CH)_2$[19] and *trans*-$L_2PtMeCl$[27] were prepared by literature methods. The reagent [*trans*-$PtL_2(Me)(acetone)]PF_6$ (**23**) was prepared by a procedure similar that reported for preparing the analogous PMe_2Ph derivative.[28]

A 0.1-mmol portion of **23** was added to an acetone suspension of 0.053 g (0.11 mmol) of **14** at 25 °C as an acetone solution. Within 15 min the acetylide reactant complex dissolved, and the reaction solution changed color from nearly colorless to pale yellow. After the solution was stirred for 6 h, the solution color had changed to orange-red. After 24 h of reaction, the solvent was removed under reduced pressure. The reaction residue was washed with three portions of hexane/ether (1:4) solution. The product was precipitated from THF/pentane solution as a dark red oil that formed a dry red solid when dried under vacuum (0.035 g, 30%): decomp pt 85–90 °C; IR (CH_2Cl_2) ν(C≡C) 2080 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90–1.20 (m, 36, PCH_2CH_3), 1.80–2.20 (m, 28, PCH_2CH_3 + C≡CMe + CH), 5.68, 6.29 (m, 1 C=CH, 2 somers). Anal. Calcd for $C_{29}H_{65}F_6P_5Pt_2$: C, 32.48; H, 6.06; P, 14.44. Found: C, 32.42; H, 5.82; P, 14.21.

Acknowledgment. C.M.L. thanks the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. **2**, 51716-77-9; **3a**, 106357-35-1; **3b**, 106357-37-3; **5**, 106297-59-0; **6**, 106297-61-4; **7**, 106297-65-8; **8**, 106297-69-2; **9**, 106297-67-0; **10**, 106319-58-8; **11**, 106297-63-6; **12**, 106297-71-6; **13**, 106297-57-8; **14**, 34230-58-5; **15**, 34230-61-0; **16**, 12308-30-4; **17**, 97086-92-5; **18**, 87960-48-3; **19**, 69140-93-8; **20**, 18533-63-6; **21**, 31386-97-7; **23**, 106297-72-7; Pt, 7440-06-4; Fe, 7439-89-6; Au, 7440-57-5; W, 7440-33-7; Ni, 7440-02-0; Pd, 7440-05-3.

(27) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1959**, 705–716.
(28) Chisholm, M. H.; Clark, H. C. *J. Am. Chem. Soc.* **1972**, *94*, 1532–1539.

Stereochemistry of Diastereoisomeric Complexes *cis*-Dichloro[(*S*)-α-methylbenzylamine][(*S*,*S*)- or (*R*,*R*)-2-vinyltetrahydropyran]platinum(II)

Gloria Uccello-Barretta, Raffaello Lazzaroni, Carlo Bertucci, and Piero Salvadori*

Centro di Studio del CNR per le Macromolecole Stereordinate ed Otticamente Attive, Dipartimento di Chimica e Chimica Industriale, 56100 Pisa, Italy

Received December 4, 1985

The stereochemistry in solution of the diastereoisomeric complexes *cis*-dichloro[(*S*)-α-methylbenzylamine][(*S*)-2-vinyl-(*S*)-tetrahydropyran]platinum(II) and *cis*-dichloro[(*S*)-α-methylbenzylamine][(*R*)-2-vinyl-(*R*)-tetrahydropyran]platinum(II) was established by circular dichroism, ^1H NMR, and ^{195}Pt NMR investigations. In both diastereoisomers an intramolecular hydrogen bond, N–H···O, between the amine group and the oxygen atom of the 2-vinyltetrahydropyran determines the stereochemistry of the complexes in solution.

Introduction

A number of studies have been made on chiral dichloro(amine)(olefin)platinum(II) complexes undertaken to elucidate the stereochemistry of coordinated ligands in solution.[1-5]

Repulsive steric interactions were claimed as responsible for the enantioface differentiation in the coordination of the olefin to the metal.[1,2] The presence of an oxygen atom in the case of unsaturated ethers can introduce a nonbonding electron repulsive interaction with chlorine atoms or/and an attractive interaction via the intramolecular hydrogen bond with a cis amine group,[6-8] making the stereochemistry of coordinated ligands very different.

Recently two diastereoisomeric complexes containing a chiral amine and a chiral allyl ether as organic ligands, namely, *cis*-dichloro[(*S*)-α-methylbenzylamine][(*S*)-2-vinyltetrahydropyran]platinum(II) (**1**) and *cis*-dichloro-[(*S*)-α-methylbenzylamine][(*R*)-2-vinyltetrahydropyran]-platinum(II) (**2**), have been prepared,[9] and the molecular structure of **1** in the solid state has been studied by X-ray analysis.[10]

We found it extremely interesting to compare the stereochemistry of the two diastereoisomeric complexes **1** and **2** arising from the two enantiomers of a vinyl derivative in the frame of the investigations on the origin of the stereospecificity observed in some important catalytic organic reactions such as hydroformylation, hydrogenation, and stereospecific polymerization. Indeed the aforementioned Pt(II) complexes can be taken as models of the coordination step of the enantiomer pair to the same asymmetric catalytic center in order to get information on the reactive intermediates that are of value for the stereochemical pathway of the reaction.

In this paper we established the stereochemistry in solution of the diastereoisomeric complexes **1** and **2** by circular dichroism (CD) and NMR, pointing out the role played by intramolecular interactions on the conformational arrangement of the ligands and assigning the ab-

(1) Panunzi, A.; Paiaro, G. *J. Am. Chem. Soc.* **1966**, *88*, 4844.
(2) Paiaro, G.; Corradini, P.; Palumbo, R.; Panunzi, A. *Makromol. Chem.* **1964**, *71*, 184.
(3) Lazzaroni, R.; Salvadori, P.; Pino, P. *J. Chem. Soc., Chem. Commun.* **1970**, 1164.
(4) Lazzaroni, R.; Bertozzi, S.; Bertucci, C.; Salvadori, P.; Pino, P. *J. Isr. Chem.* **1976/1977**, *15*, 63.
(5) Shinoda, S.; Yamaguchi, Y.; Saito, Y. *Inorg. Chem.* **1979**, *18*, 674.
(6) Sartori, F.; Leoni, L.; Lazzaroni, R.; Salvadori, P. *J. Chem. Soc., Chem. Commun.* **1974**, 322.
(7) Lazzaroni, R.; Uccello-Barretta, G.; Bertozzi, S.; Salvadori, P. *J. Organomet. Chem.* **1984**, *275*, 145.
(8) Lazzaroni, R.; Uccello-Barretta, G.; Bertozzi, S.; Salvadori, P. *J. Organomet. Chem.* **1985**, *297*, 117.
(9) Lazzaroni, R.; Uccello-Barretta, G.; Pini, D.; Pucci, S.; Salvadori, P. *J. Chem. Res. Synop.* **1983**, 286.
(10) Lazzaroni, R.; Uccello-Barretta, G.; Bertozzi, S.; Bertucci, C.; Marchetti, F. *J. Chem. Res. Synop.* **1984**, 286.

0276-7333/87/2306-0550$01.50/0