has to be attributed to the quickness of the monoanion destruction rather than to the irreversibility of the heterogeneous charge transfer; in addition it seems likely that the electrode formation of the dianion takes place at potentials more negative than the solvent discharge itself. Also in this case a reoxidation peak, indicative of the decomposition of the cluster anion, is present in the reverse scan at about −0.3 V, well anodic to the cathodic peak.

Finally compounds VII and VIII reduce through similar cathodic processes involving one two-electron step. In both cases the relevant cathodic peak shows the typical features due to a charge transfer totally irreversible in character. As an example Figure 10 shows the response from VII.

Thus the electrochemical reduction process of μ_3-η^2-$\|$-alkyne clusters results to be completely irreversible, giving rise to a rapid declusterification. This is consistent with the EHMO picture of Schilling and Hoffman:[4] for a 48-electron species just a highly destabilized asymmetric MO (having metal–metal antibonding character due to its parentage with the $2e_a$ orbital) is available, so the added electrons cause strong destabilization of the entire polyhedral frame.

Experimental Section

The $Fe_3(CO)_9(RC_2R)$ (I–IV) clusters were synthesized from $Fe_3(CO)_{12}$ and the appropriate alkyne in 1:1 molecular ratio in *n*-hexane at reflux under N_2 for 4 h (MeC_2Me and EtC_2Et) or 6 h (PhC_2Me and PhC_2Ph). The separations of the reaction mixture were carried out on TLC plates (SiO_2, eluant petroleum ether–diethyl ether, 9:1 v/v). The preparation of ^{13}CO-enriched samples of $Fe_3(CO)_9(RC_2R)$ complexes was performed by a similar procedure using $Fe_3(CO)_{12}$, ~20% enriched in ^{13}CO, as the starting material.

Compounds V–VIII were synthesized according to the published procedures.[9,30,31] After crystallization in *n*-heptane at 0 °C, purity of all tested complexes was checked by IR and ^1H and ^{13}C NMR spectroscopy.

The IR spectra were recorded on a Perkin-Elmer 580 B instrument and the ^1H and ^{13}C NMR on a JEOL GX-270-89 machine (for variable-temperature ^1H NMR experiments a JEOL C-60-HL was also employed).

The electrochemical apparatus has been described elsewhere.[34] Potential values refer to a saturated aqueous calomel electrode (SCE). The temperature was controlled at 20 ± 0.1 °C. The exhaustive macroelectrolysis of $Fe_3(CO)_9(EtC_2Et)$ (I) was brought about at the controlled potential of −1.0 V by using a platinum gauze working macroelectrode. As the two-electron reduction proceeds, the solution turns from brown into dark-red. All the manipulations of the electrogenerated $[Fe_3(CO)_9(EtC_2Et)]^{2-}$ dianion were carried out in a glovebox purged with dry dinitrogen. The solvents used for electrochemistry, dichloromethane and acetone, were from Burdick and Jackson, were "distilled in glass", and were used without purification. Tetrabutylammonium perchlorate (TBAP, Fluka) and tetraethylammonium perchlorate (TEAP, Carlo Erba) supporting electrolytes were dried in a vacuum oven and used without further purification. Lithium perchlorate and sodium perchlorate supporting electrolytes were prepared by neutralizing perchloric acid with the corresponding alkali carbonate, twice crystallizing from methanol, and finally drying at 110 °C. Bis(η^5-cyclopentadienyl)iron(II) (ferrocene, Alfa Products) was used as purchased. Extra pure dinitrogen was employed to remove oxygen from tested solutions.

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Registry No. I, 69402-19-3; II, 12171-93-6; III, 101315-98-4; IVa, 101315-99-5; IVb, 101316-00-1; V, 78109-40-7; VI, 101316-01-2; VII, 80303-37-3; VIII, 101316-02-3; $[Fe_3(CO)_9(EtC_2Et)][NBu_4]_2$, 101316-04-5; $[Fe_3(CO)_9(EtC_2Et)][NEt_4]_2$, 101316-05-6; $[Fe_3(CO)_9(EtC_2Et)]Li_2$, 101400-35-5; $[Fe_3(CO)_9(EtC_2Et)]Na_2$, 101316-06-7; Fe, 7439-89-6; Os, 7440-04-2.

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Methyl–Ethylene and Methyl–Carbonyl Complexes of Platinum(II) and Platinum(IV)

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The methyl(ethylene)platinum(II) complex $[Pt_2(\mu\text{-}Cl)_2Me_2(C_2H_4)_2]$ and methylcarbonylplatinum(II) complex $[Pt_2(\mu\text{-}Cl)_2Me_2(CO)_2]$ have been prepared and characterized. Reactions of $[Pt_2(\mu\text{-}Cl)_2Me_2(C_2H_4)_2]$ with alkenes or alkynes (un) generally give the products of substitution $[Pt_2(\mu\text{-}Cl)_2Me_2(un)_2]$, but $CF_3C{\equiv}CCF_3$ gives insertion into the PtMe bond. Reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ with ethylene yields the dimethyl(ethylene)platinum(II) complex *cis*-$[PtMe_2(SMe_2)(C_2H_4)]$ and with carbon monoxide *cis*-$[PtMe_2(SMe_2)(CO)]$ is formed. Oxidative addition of iodomethane to *cis*-$[PtMe_2(CO)(SMe_2)]$ produces a rare example of a platinum(IV) carbonyl complex *fac*-$[PtIMe_3(SMe_2)(CO)]$.

Introduction

This paper reports the synthesis, characterization, and properties of several compounds containing *cis*-methyl(ethylene)platinum(II) or *cis*-methylcarbonylplatinum(II) units. Such compounds are unusual, although some interesting examples such as *cis*-$[PtMe(C_2H_4)(diars)]^+$, diars = $1,2\text{-}(Me_2As)_2C_6H_4$, and *cis*-$[PtMe_2(CO)_2]$ are known[1–3] and are of interest as models for catalytic intermediates.[4–6] This work was developed from an observation that reaction

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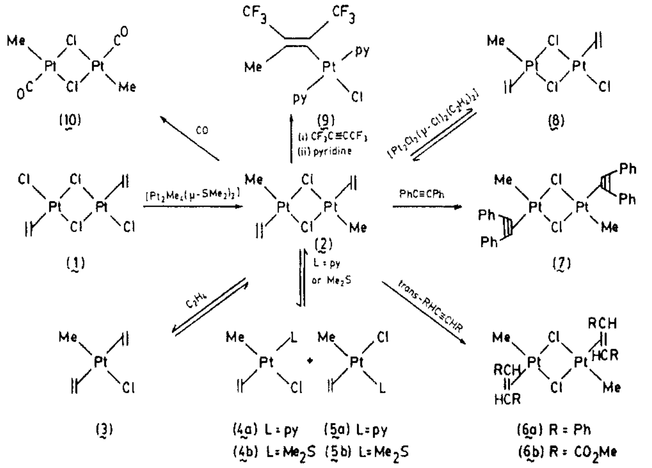
Scheme I



of *cis*-$[PtMe_2(SMe_2)_2]$ with Zeise's dimer $[Pt_2(\mu\text{-}Cl)_2Cl_2(C_2H_4)_2]$ gave the complex $[Pt_2(\mu\text{-}Cl)_2Me_2(C_2H_4)_2]$ by methyl for chloro exchange between platinum centers.[7,8] A preliminary account has been published.[8]

Results and Discussion

Synthesis and Characterization of $[Pt_2(\mu\text{-}Cl)_2Me_2(C_2H_4)_2]$. The new methyl(ethylene)platinum complex was prepared by methylation of Zeise's dimer $[Pt_2(\mu\text{-}Cl)_2Cl_2(C_2H_4)_2]$ (1) with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$[7] in the presence of excess ethylene (Scheme I). The desired product 2 was separated from the second product $[Pt_2(\mu\text{-}Cl)_2Me_2(SMe_2)_2]$ by chromatography on a Florisil column, when only 2 passed through the column. We have shown previously that $[Pt_2(\mu\text{-}Cl)_2Me_2(SMe_2)_2]$ is thermally unstable,[7] and it is decomposed on the column. However, this complex is sufficiently stable to be positively characterized by its ^1H NMR spectrum in the reaction mixture. Yields of 2 of 90% could be obtained from this reaction.

Complex 2 could also be prepared by reaction of Zeise's dimer with *cis*-$[PtMe_2(SMe_2)_2]$, when the byproduct was *trans*-$[PtClMe(SMe_2)_2]$, and with $SnMe_4$, when the byproduct was $SnClMe_3$. However, isolated yields were much lower due partly to decomposition reactions (e.g., with $SnMe_4$) or to problems with purification of 2 (e.g., with $[PtMe_2(SMe_2)_2]$). Therefore the methylating agent $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$, although expensive, was preferred in the synthesis of 2. More powerful methylating agents such as MeLi or MeMgCl led to decomposition of Zeise's dimer, and this is probably why the complex 2 has not been successfully prepared earlier.

Complex 2 was characterized by elemental analysis and by its ^1H and ^{13}C NMR spectra.[8] Of particular significance is the observation of satellites around the C_2H_4 resonance in the ^1H or ^{13}C NMR spectra at room temperature in CD_2Cl_2 solution showing that rapid reversible dissociation of C_2H_4 does not occur. Above −65 °C, the ethylene resonance in the ^1H NMR spectrum of 2 appears as a singlet with ^{195}Pt coupling, but below −65 °C this resonance splits into an [AA′BB′] pattern with ^{195}Pt coupling. This effect has been observed previously in $[PtCl(acac)(C_2H_4)]$ and related complexes[9] and is due to the freezing out of rotation about the $Pt–C_2H_4$ bond.[4]

In contrast Zeise's dimer gives a broad singlet without ^{195}Pt satellites at temperatures as low as −90 °C in CD_2Cl_2 solution, indicating a very rapid exchange process. We suggest that the strong σ-donor methyl group leads to stronger $Pt–C_2H_4$ back-bonding in 2 and hence the ethylene is less prone to dissociation or rotation compared to Zeise's dimer.[10]

Reactions of $[Pt_2(\mu\text{-}Cl)_2Me_2(C_2H_4)_2]$. (a) With Pyridine and Dimethyl Sulfide. A common method for preparing monomeric olefin complexes of platinum(II) involves reaction of a halogen-bridged dimer $[Pt_2(\mu\text{-}X)_2X_2(olefin)_2]$ with a neutral ligand.[11] When 2 was treated with a stoichiometric quantity of pyridine, two isomers of $[PtClMe(C_2H_4)(py)]$ (**4a** and **5a**) were easily isolated, thus confirming the dimeric structure of 2. $[PtCl_2(C_2H_4)(py)]$ exists only as the trans isomer,[12] but the presence of two of the three possible isomers of $[PtClMe(C_2H_4)(py)]$ was evident from two distinct sets of Pt–Me, $Pt–C_2H_4$, and pyridine Hα resonances in the ^1H NMR spectrum. Isomers **4a** and **5a** were present in a ratio of 3:1, and the structures were deduced from the magnitudes of *J*(PtH) coupling constants.[1-4,12] Isomer **4a** gave signals in the ^1H NMR spectrum due to the C_2H_4 and pyridine H_α protons which had satellites due to coupling to ^{195}Pt, but no such satellites were observed for the corresponding resonances of isomer **5a**. This is presumably due to labilization of pyridine by the high trans influence of the methyl group which leads to ligand exchange[4,12] but which does not lead to equilibration with **4a**.

A similar reaction of 2 with Me_2S gave **4b** and **5b** as major products, but a disproportionation occurred on evaporation of the reaction mixture at room temperature to give 2 and *trans*-$[PtClMe(SMe_2)_2]$. The mixture of **4b** and **5b** could be isolated by evaporation of the solvent from the reaction mixture at −78 °C, but the solid product was thermally unstable at room temperature.

(b) With Alkenes and Alkynes. In CD_2Cl_2 solution at 35 °C in the presence of a large excess of ethylene, complex 2 apparently remains dimeric and undergoes rapid exchange of free and coordinated ethylene, as is evident from the unchanged MePt resonance in the ^1H NMR spectrum and a broad $(C_2H_4)Pt$ resonance (shifted upfield from free ethylene) possessing no ^{195}Pt satellites. At −60 °C there are two distinct MePt resonances; one can be attributed to complex 2 while the other, having a lower coupling constant, $^2J(PtH)$ = 68 Hz, is due to *trans*-$[PtClMe(C_2H_4)_2]$ (3). It is evident that the monomeric species exists in equilibrium with complex 2 at low temperatures. The rapid exchange of free and coordinated ethylene in 2 at room temperature presumably occurs by rapid reversible formation of 3, though the NMR parameters show that very little 3 is present at room temperature. Chatt has prepared the analogous complex $[PtCl_2(C_2H_4)_2]$ by reaction of Zeise's dimer with ethylene and other dichlorobis(olefin)platinum(II) monomeric complexes have also been prepared.[13]

Reaction of 2 with *trans*-stilbene or dimethyl fumarate gave the corresponding alkene complexes **6a** or **6b** by displacement of ethylene. These complexes were isolated as yellow-orange solids, but they decomposed in 1–2 days at room temperature. In solution the ^1H NMR spectra contained broad singlets due to the alkene protons at room

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(8) Scott, J. D.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1984**, 193.

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(10) Compare *cis*-$[PtMe(C_2H_4)(diars)]^+$, in which the ethylene is more labile than in *trans*-$[PtMe(C_2H_4)(PMe_2Ph)_2]^+$ and related complexes.[1]

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(13) Chatt, J. *J. Chem. Soc.* **1951**, 652. Chatt, J.; Wilkins, R. G. *J. Chem. Soc.* **1952**, 2622. Jonassen, H. B.; Field, J. E. *J. Am. Chem. Soc.* **1957**, *79*, 1275. Harrod, J. F. *Inorg. Chem.* **1965**, *4*, 428.

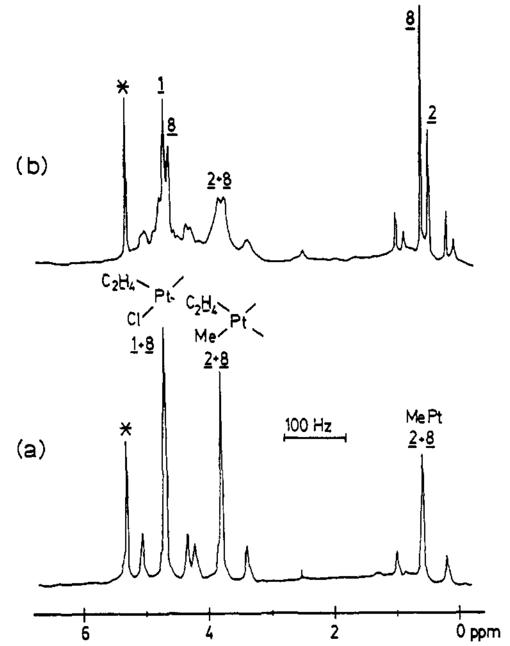


Figure 1. ^1H NMR spectra (100 MHz) of a 1:1 mixture of complexes 1 and 2 in CD_2Cl_2, to give an equilibrium mixture with 8: (a) at −20 °C, in the fast-exchange regime; (b) at −80 °C, in the slow-exchange regime and with slow rotation about the Pt–C_2H_4 bonds for 2 and 8. The peak marked asterisk is due to $CHDCl_2$.

temperature, indicating a rapid exchange process, but at −90 °C coupling to ^{195}Pt was observed and the signals appeared as an [AB] quartet. Thus at low temperature alkene exchange and rotation about the Pt–alkene bond can be frozen out.

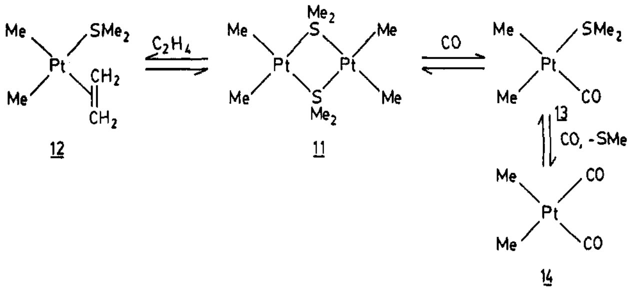
The diphenylacetylene complex 7 was easily prepared by reaction of 2 with diphenylacetylene, but similar reactions with but-2-yne or phenylacetylene gave polymeric materials and it was not possible to identify the platinum-containing products. A similar reaction of Zeise's dimer with diphenylacetylene led to rapid reduction to metallic platinum,[14] and again it seems that the presence of the σ-donor methyl group enhances the stability of 7 by increasing the platinum–alkyne d_π–p_π back-bonding.

The activated alkyne $CF_3C{\equiv}CCF_3$ reacted rapidly with 2, and, after treatment with pyridine, complex 9 was obtained. Considerable polymer was also formed. The cis insertion is proved by the magnitude of the coupling ^5J(FF) = 15 Hz, which is typical of this stereochemistry and much larger than for the trans isomer.[15]

In general, substitution of ethylene in 2 for other alkenes or alkynes is very easy and presumably occurs by way of intermediates analogous to 3. This ease of substitution is also partly responsible for the rapid insertion of $CF_3C{\equiv}CCF_3$ into the Pt–Me bond[16] and for the easy polymerization of some alkynes by 2. Reaction of 2 with excess ethylene at 50 °C leads to formation of some low molecular weight polyethylene, but, since some decomposition of 2 occurs under these conditions, it is not clear that 2 is the active catalyst for this process.

(c) With Carbon Monoxide. Carbon monoxide displaced ethylene from 2 to give the methylcarbonylplatinum derivative 10, which could be isolated as a colorless solid but which decomposed at room temperature in about 0.5 day. Complex 10 was characterized by a carbonyl stretch, ν(CO) = 2040 cm^{-1} (CH_2Cl_2 solution), in the IR, by a methylplatinum resonance in the ^1H NMR at δ 1.24 (^2J(PtH) = 76 Hz) in CD_2Cl_2, and by the mass spectrum, which gave a parent ion at m/e 546 with the expected isotope pattern for a Pt_2Cl_2 derivative. The analogous complex $[Pt_2(\mu\text{-}Cl)_2Cl_2(CO)_2]$[17] has ν(CO) = 2146 cm^{-1}, indicating weaker back-bonding than in **10** as expected from the earlier discussion. There are very few methylcarbonylplatinum(II) complexes, and **10** appears to be the first binuclear derivative.[5,6]

Scheme II



(d) With Zeise's Dimer. Reaction of equimolar amounts of complex 2 and Zeise's dimer 1 leads to rapid equilibration with the unsymmetrical dimer 8. At temperatures above −50 °C this equilibration was rapid on the NMR time scale, as illustrated by Figure 1a. The spectrum shows methylplatinum, (ethylene)platinum cis to Me, and (ethylene)platinum cis to Cl signals with the expected intensity ratios. This spectrum is consistent either with the pure complex 8 or with a rapidly equilibrating mixture of 8, 1, and 2, occurring by rapid exchange of $PtClMe(C_2H_4)$ and $PtCl_2(C_2H_4)$ fragments. That the latter interpretation is correct is shown by the spectrum at −80 °C shown in Figure 1b. Separate resonances are clearly seen for the methylplatinum groups of 2 and 8. The ethylene resonances are less clearly resolved because rotation about Pt–C_2H_4 bonds is also frozen out for complexes 2 and 8. However, the singlet due to 1 is resolved from the $[A_2B_2]$ multiplet of the $Pt(C_2H_4)Cl$ resonance of 8 under these conditions. Integration indicates that 1, 8, and 2 are present in approximately the expected statistical ratio of 1:2:1 at −80 °C.

Synthesis of *cis*-$[PtMe_2(C_2H_4)(SMe_2)]$ and *cis*-$[PtMe_2(CO)(SMe_2)]$. Reaction of *cis*-$[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (11) with ethylene in CD_2Cl_2 solution gave an equilibrium mixture of the reagents and *cis*-$[PtMe_2(C_2H_4)(SMe_2)]$ (12; Scheme II), but only 11 was recovered on evaporation of such solutions.

The cis stereochemistry is shown by the observation of two *Me*Pt resonance in the ^1H NMR spectrum of 12, as well as by the very low coupling constants, $^3J(PtSMe_2)$ = 21 Hz and $^2J(PtC_2H_4)$ = 37 Hz for the methylsulfur and ethylene resonances. The equilibrium constant changes with temperature as is clearly shown by Figure 2. Although exchange between free and coordinated ethylene was slow on the NMR time scale at 35 °C, rotation about the Pt–C_2H_4 bond appeared to be fast even at −90 °C since a singlet for the coordinated ethylene of *12* was observed at all temperatures.

No products analogous to 12 could be detected from reactions of diphenylacetylene or *trans*-stilbene with 11 even at low temperatures. Clearly, there is a fine balance as to whether the dimer 11 or the monomeric complexes analogous to 12 will be preferred in this system.

Carbon monoxide is a stronger ligand, and reaction with 11 gave both 13 and 14 (Scheme II). Complex 14 has been

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[14] Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939. Chatt, J.; Guy, R. G.; Duncanson, L. A. *J. Chem. Soc.* **1961**, 827.

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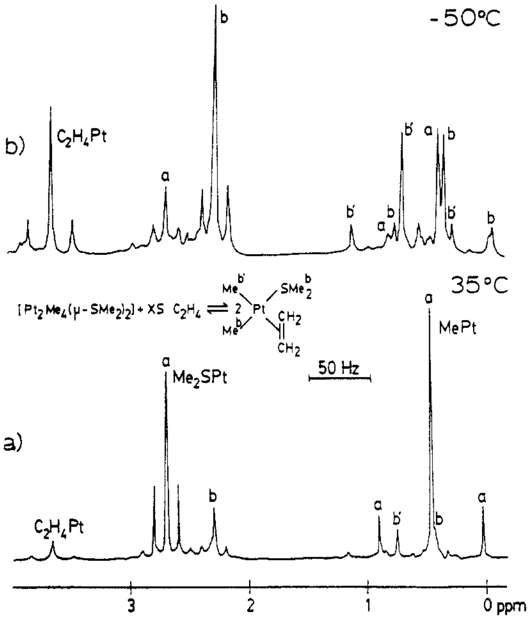
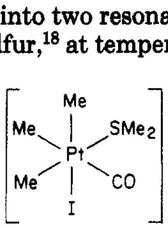


Figure 2. ^1H NMR spectra (100 MHz) of a mixture of $[Pt_2Me_4(\mu-SMe_2)_2]$ and C_2H_4 in equilibrium with *cis*-$[PtMe_2(SMe_2)(C_2H_4)]$: (a) at 35 °C, mostly $[Pt_2Me_4(\mu-SMe_2)_2]$; (b) at −50 °C, mostly *cis*-$[PtMe_2(SMe_2)(C_2H_4)]$.

prepared previously,[2,3] and we find that **13** can be prepared in pure form by reaction of *cis*-$[PtMe_2(SMe_2)_2]$ with CO. Apparently the extra SMe_2 is sufficient to prevent further reaction of **13** with CO to give **14**.

A Methylcarbonylplatinum(IV) Complex. Oxidative addition of iodomethane to **13** gave the complex *fac*-$[PtIMe_3(CO)(SMe_2)]$ (**15**) along with byproducts *fac*-$[PtIMe_3(SMe_2)_2]$ and $[(PtIMe_3)_4]$. Complex **15** could also be prepared in solution by reaction of *fac*-$[PtIMe_3(SMe_2)_2]$ with excess CO. It appears to be the first example of a methylcarbonylplatinum(IV) complex. Complex **15** is characterized by a carbonyl stretching frequency, $\nu(CO) = 2090\ cm^{-1}$ in benzene, and by the observation of three MePt and one Me_2S resonances in the ratio 1:1:1:2, respectively. The methylplatinum group trans to CO had a lower value for $^2J(PtCH_3) = 64$ Hz than those trans to iodide or SMe_2, each of which gave $^2J(PtCH_3) = 70$ Hz, due to the higher trans influence of CO. The methylsulfur resonance of **15** split into two resonances, due to freezing out of inversion at sulfur,[18] at temperatures below −20 °C.



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Conclusions

A number of new but very simple complexes containing *cis*-$PtMe(C_2H_4)$ and *cis*-PtMe(CO) groups have been obtained. The ethylene complexes were only found with platinum(II), but carbonyl derivatives of both platinum(II) and platinum(IV) were observed. Many of the complexes were thermally unstable, but they could be characterized unambiguously by low-temperature NMR studies. Only with the activated alkyne $CF_3C{\equiv}CCF_3$ did insertion of the unsaturated group into the Pt—Me bond occur.

Experimental Section

The ^1H, ^{19}F, and $^{13}C\{^1H\}$ NMR spectra were recorded on Varian XL100 and XL200 spectrometers. ^1H and ^{13}C chemical shifts were measured relative to Me_4Si, and the ^{19}F chemical shifts were measured relative to $CFCl_3$.

Infrared spectra were recorded by using NaCl solution cells on a Beckman 4250 spectrophotometer.

Gas chromatographic analyses were performed on a Varian 1400 gas chromatograph equipped with a porapak Q column.

Elemental analyses were performed by Guelph Chemical Laboratories, Ltd., Guelph, Ontario.

Complexes $[Pt_2Me_4(\mu-SMe_2)_2]$ and $[Pt_2(\mu-Cl)_2Cl_2(C_2H_4)_2]$ were prepared by modifications of known procedures.[7,19]

Synthesis of $[Pt_2(\mu-Cl)_2Me_2(C_2H_4)_2]$. $[Pt_2(\mu-Cl)_2Cl_2(C_2H_4)_2]$ (0.3502 g, 0.5955 mmol) was suspended in CH_2Cl_2 (40 mL) saturated with C_2H_4 at 0 °C. $[Pt_2Me_4(\mu-SMe_2)_2]$ (0.3422 g, 0.5955 mmol) in CH_2Cl_2 (20 mL) was added to the stirred solution. The solution was warmed slowly to room temperature and allowed to react for 0.5 h. The solvent volume was reduced to ~5 mL, and the mixture was added to a 12-in. column packed with Florisil and eluted with CH_2Cl_2 (50 mL). The solvent was removed, yielding a white solid identified as $[Pt_2(\mu-Cl)_2Me_2(C_2H_4)_2]$ (0.2837 g, 91%); mp 77–90 °C dec. Anal. Calcd for $[Pt_2(\mu-Cl)_2Me_2(C_2H_4)_2]$: C, 13.17; H, 2.58. Found: C, 13.30; H, 2.57. NMR in CD_2Cl_2, 35 °C: ^1H, δ 0.52 [s, $^2J(PtH) = 81$ Hz, *Me*Pt], 3.73 [s, $^2J(PtH) = 79$ Hz, $(C_2H_4)Pt$]; ^{13}C, δ −8.63 [s, $^1J(PtC) = 682$ Hz, *Me*Pt], 63.38 [s, $^1J(PtC) = 254$ Hz, $(C_2H_4)Pt$]. At low-temperatures (below −65 °C) the $(C_2H_4)Pt$ resonances in the ^1H NMR resolved into an $[AB]_2$ multiplet (see ref 8).

Preparation of $[PtClMe(C_2H_4)(py)]$. $[Pt_2(\mu-Cl)_2Me_2(C_2H_4)_2]$ (0.1156 g, 0.2112 mmol) was dissolved in CH_2Cl_2 (10 mL), and pyridine (0.0334 g, 0.4224 mmol, 34.0 μL) was added as a CH_2Cl_2 solution (5 mL) at 0 °C. The solution immediately turned clear yellow, and the product identified as $[PtClMe(C_2H_4)(py)]$ was isolated as a yellow solid (0.1402, 98%) by concentration and then precipitation using *n*-pentane; mp 64–72 °C dec. Anal. Calcd for $[PtClMe(C_2H_4)(py)]$: C, 27.24; H, 3.43. Found: C, 27.73; H, 3.53. ^1H NMR in CD_2Cl_2: **4a**, δ 0.66 [s, $^2J(PtH) = 72$ Hz, *Me*Pt], 3.53 [s, $^2J(PtH) = 72$ Hz, (C_2H_4) Pt]; **5a**, δ 0.41 [s, $^2J(PtH) = 76$ Hz, *Me*Pt], 4.12 [s, $^2J(PtH)$ not resolved, $(C_2H_4)Pt$].

Preparation of $[PtClMe(SMe_2)(C_2H_4)]$. $[Pt_2(\mu-Cl)_2Me_2(C_2H_4)_2]$ (0.1251 g, 0.2286 mmol) was dissolved in CH_2Cl_2 (10 mL), and 2 equiv of SMe_2 (0.02841 g, 0.4572 mmol, 33.6 μL) was added as a CH_2Cl_2 solution (5 mL) at 0 °C. The solution immediately turned clear yellow and was cooled rapidly to −78°C. Removal of the solvent at −78 °C yields the thermally unstable beige solid identified as $[PtClMe(SMe_2)(C_2H_4)]$ (0.1443 g, 94%); mp 30–39 °C dec. Anal. Calcd for $[PtClMe(SMe_2)(C_2H_4)]$: C, 17.88; H, 3.90. Found: C, 17.66; H, 4.17. ^1H NMR in CD_2Cl_2, −80 °C: **4b**, δ 0.53 [s, $^2J(PtH) = 70$ Hz, *Me*Pt], 3.62 [s, $^2J(PtH) = 72$ Hz, $(C_2H_4)Pt$], 2.43 [s, $^3J(PtH) = 16$ Hz, $(Me_2S)Pt$]; **5b**, δ 0.74 [s, $^2J(PtH) = 74$ Hz, *Me*Pt], 3.73 [s, $^2J(PtH) = 72$ Hz, $(C_2H_4)Pt$], 2.53 [s, $^3J(PtH) = 22$ Hz, $(Me_2S)Pt$].

Reaction of $[Pt_2(\mu-Cl)_2Me_2(C_2H_4)_2]$ with Ethylene. (A) A solution of $[Pt_2(\mu-Cl)_2Me_2(C_2H_4)_2]$ (0.0543 g, 0.09921 mmol) in CD_2Cl_2 (1.5 mL) in an NMR tube was degassed on the vacuum line, a large excess of C_2H_4 was condensed into the tube, and the tube was sealed. Low-temperature ^1H NMR showed conversion to *trans*-$[PtClMe(C_2H_4)_2]$. ^1H NMR in CD_2Cl_2, −60 °C: δ 0.32 [s, $^2J(PtH) = 68$ Hz, *MePt*], 3.62 [s, $^2J(PtH)$ not resolved, $(C_2H_4)Pt$].

(B) A solution of $[Pt_2(\mu-Cl)_2Me_2(C_2H_4)_2]$ (0.1304 g, 0.2383 mmol) in dry benzene (100 mL) was stirred at 50 °C for 20 h under 10 atm of C_2H_4 in a pressure reactor. A clear colorless solution was obtained, but decomposition giving an insoluble black solid (possibly Pt and $PtCl_2$) occurred on partial evaporation of the solution to a volume of 25 mL. The solids were filtered off (0.0158 g), leaving a clear yellow solution which when evaporated to dryness yielded a yellow solid (0.1417 g). This product easily dissolved in $CDCl_3$ (2 mL), and the ^1H NMR showed the presence of both $[Pt_2(\mu-Cl)_2Me_2(C_2H_4)_2]$ and low molecular weight polyethylene: δ 1.25 [s, $(CH_2)_n$]; 0.84 [t, CH_3].

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Preparation of $[Pt_2(\mu\text{-}Cl)_2Me_2(PhC{\equiv}CPh)_2]$. $[Pt_2(\mu\text{-}Cl)_2Me_2(C_2H_4)_2]$ (0.0801 g, 0.1464 mmol) was dissolved in CH_2Cl_2 (5 mL), and $PhC{\equiv}CPh$ (0.0521 g, 0.2928 mmol) in CH_2Cl_2 (5 mL) was added at 0 °C. The colorless solution immediately turned clear orange. The mixture was allowed to warm to room temperature, and evaporation of the solvent yielded an orange solid identified as $[Pt_2(\mu\text{-}Cl)_2Me_2(PhC{\equiv}CPh)_2]$ (0.1141 g, 92%); mp 81–90 °C dec. Anal. Calcd for $[Pt_2(\mu\text{-}Cl)_2Me_2(PhC{\equiv}CPh)_2]$: C, 42.51; H, 3.09. Found: C, 42.15; H, 2.95. ^1H NMR in CD_2Cl_2, 35 °C: δ 0.90 [s, $^2J(PtH)$ = 86 Hz, *Me*Pt], 7.44 and 8.06 [m, Ph].

Similarly were prepared complexes **6a**, yield 94%, and **6b**, yield 98%, from *trans*-stilbene and dimethyl fumarate, respectively. ^1H NMR in CD_2Cl_2: **6a** at 35 °C, δ 0.42 [s, $^2J(PtH)$ = 84 Hz, *Me*Pt], 5.96 [s, $^2J(PtH)$ not resolved, $({=}CH)Pt$]; **6a** at −90 °C, δ 0.30 [s, $^2J(PtH)$ = 84 Hz, *Me*Pt], 5.69 [m, $^2J(PtH)$ not resolved, $Pt(H_aC{=})$], 6.15 [m, $^2J(PtH)$ not resolved, $Pt(H_bC{=})$]; **6b** at −90 °C, δ 0.45 [s, $^2J(PtH)$ = 84 Hz, *Me*Pt], 4.91 [AB, $^2J(PtH)$ not resolved, $Pt(HC{=})$], 3.73 [s, O*Me*]. Anal. Calcd for $[Pt_2(\mu\text{-}Cl)_2Me_2(MeO_2CCH{=}CHCO_2Me)_2]$ (**6b**): C, 21.57; H, 2.85. Found: C, 21.46; H, 3.36. **6b**: mp 100–103 °C.

***trans*-$[PtCl\{C(CF_3){=}C(CF_3)Me\}(C_5H_5N)_2]$ (9).** Excess $CF_3C{\equiv}CCF_3$ was condensed into a tube containing a solution of $[Pt_2(\mu\text{-}Cl)_2Me_2(C_2H_4)_2]$ (0.051 g) in $CHCl_3$ (5 mL), and the tube was sealed. The tube was allowed to warm to room temperature, and, after 0.5 h, the tube was opened and the insoluble polymer was removed by filtration to give a clear solution. A solution of pyridine (0.029 g) in CH_2Cl_2 (5 mL) was added, the solution was concentrated, and pentane was added to precipitate the product as a yellow solid (0.091 g). NMR in CD_2Cl_2: ^1H, δ 1.24 [s, *Me*C]; ^{19}F, δ 40.5 [q, $^3J(PtF)$ = 93 Hz, $^5J(FF)$ = 15 Hz, (F_3CCPt)], 54.8 [q, $^5J(FF)$ = 15 Hz, (F_3CCCPt)].

Preparation of $[Pt_2(\mu\text{-}Cl)_2Me_2(CO)_2]$. Carbon monoxide was bubbled through a solution of $[Pt_2(\mu\text{-}Cl)_2Me_2(C_2H_4)_2]$ (0.1055 g, 0.1928 mmol) in CH_2Cl_2 (10 mL) for 5 min at 0 °C. The solution was filtered, and the solvent was removed from the filtrate to yield the product as a white solid (0.0981 g, 93%). The complex was thermally unstable both as a solid and in solution above 0 °C. NMR in CD_2Cl_2: δ 1.24 [s, $^2J(PtH)$ = 76 Hz, *Me*Pt]. IR in CH_2Cl_2: $\nu(CO)$ 2040 cm^{-1}.

Preparation of *cis*-$[PtMe_2(SMe_2)(CO)]$. $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (0.1078 g, 0.1876 mmol) was dissolved in acetone (10 mL), and SMe_2 (0.0233 g, 0.3752 mmol, 27.6 μL) was added to generate *cis*-$[PtMe_2(SMe_2)_2]$. Carbon monoxide was bubbled through the solution for 5 min. Evaporation of the solvent gave the *product* as a beige oil which could not be solidified. IR in acetone: $\nu(CO)$ 2030 cm^{-1}. ^1H NMR in acetone-d_6 at 35 °C: δ 0.22 [*s*, $^2J(PtH)$ = 78 Hz, *Me*Pt trans to CO], 0.76 [*s*, $^2J(PtH)$ = 89 Hz, *Me*Pt trans to SMe_2], 2.68 [*s*, $^2J(PtH)$ = 26 Hz, $(Me_2S)Pt$].

Preparation of *fac*-$[PtIMe_3(SMe_2)(CO)]$ (15). (a) *cis*-$[PtMe_2(SMe_2)(CO)]$ (0.3752 mmol) was prepared as described above in acetone-d_6 (5 mL), and iodomethane (23.5 μL) was added to the solution. The reaction was complete after 1 day giving *fac*-$[PtIMe_3(SMe_2)(CO)]$ and byproducts *fac*-$[PtIMe_3(SMe_2)_2]$ and $[(PtIMe_3)_4]$. (b) *fac*-$[PtIMe_3(SMe_2)_2]$ (0.3752 mmol) was generated in acetone-d_6 (5 mL) by addition of iodomethane (23.5 μL) to *cis*-$[PtMe_2(SMe_2)_2]$ (0.3752 mmol). CO was bubbled through the solution for 1 min. ^1H NMR in acetone-d_6 at −10 °C showed that Me_2S had been displaced by CO to generate *fac*-$[PtIMe_3(SMe_2)(CO)]$. ^1H NMR in acetone-d_6 for **15** at −10 °C: δ 1.31 [s, ,$^2J(PtH)$ = 70 Hz, *Me*Pt trans to I or SMe_2], 1.46 [s, $^2J(PtH)$ = 70 Hz, *Me*Pt trans to I or SMe_2], 1.20 [s, $^2J(PtH)$ = 64 Hz, *Me*Pt trans to CO], 2.72 [s, $^3J(PtH)$ = 14.5 Hz, $(Me_2S)Pt$]. The same reaction can be performed in benzene, but the addition of iodomethane to *cis*-$[PtMe_2(SMe_2)_2]$ is slow in this solvent. IR in benzene for **15**: $\nu(CO)$ 2090 cm^{-1}.

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Registry No. 1, 12073-36-8; 2, 90523-12-9; 3, 90523-14-1; **4a**, 90523-13-0; **4b**, 90523-20-9; **5a**, 90582-02-8; **5b**, 90582-03-9; **6a**, 90523-15-2; **6b**, 90523-16-3; 7, 90523-17-4; 8, 90523-18-5; 9, 90523-19-6; 10, 101654-06-2; 11, 79870-64-7; 12, 101654-07-3; 13, 101654-08-4; 15, 101654-09-5; $CF_3C{\equiv}CCF_3$, 692-50-2; *cis*-$[PtMe_2(SMe_2)_2]$, 87145-38-8; *fac*-$[PtIMe_3(SMe_2)_2]$, 96413-69-3; polyethylene, 9002-88-4.

Effects of Ultrasonic Waves on the Generation and Reactivities of Some Metal Powders

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Ultrasound substantially accelerates the lithium reductions of a variety of metal halides to metal powders. Zinc powder produced in approximately 40 min at room temperature with ultrasound demonstrates reactivity in the Reformatsky reaction which rivals zinc produced in 4 h with potassium in refluxing tetrahydrofuran. Similarly copper and nickel powders produced in approximately 40 min with ultrasound promote Ullman coupling as effectively as copper and nickel powders produced in >10 h in the presence of stirring. Results of the effect of iodide salts in the Ullman coupling of benzyl bromide are also presented.

Introduction

The field of reactive metal powders, as developed by Rieke et al., has a wide variety of synthetic applications.[1] It was found that the reduction of a metal halide with a group 1 element (i.e., Li, Na, K) in an ethereal solvent produces a metal slurry of exceptional reactivity.

$$MX_n + nA \rightarrow M^* + nAX$$

$$X = Cl, Br, I;\ A = Li, Na, K$$

Ultrasonic waves are known to accelerate a number of heterogeneous reactions, particularly reactions involving metals.[2] Recently, Suslick et al.[3] reported a method for

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