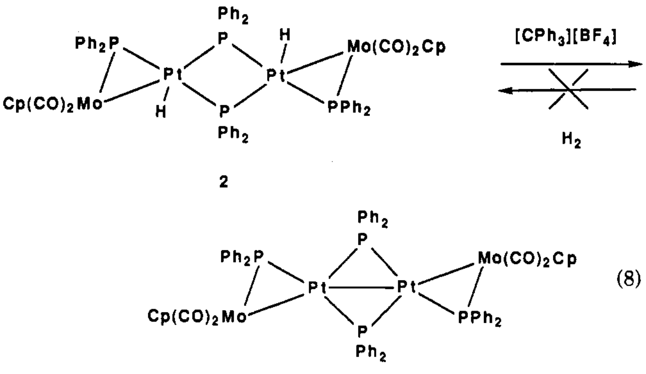

2

(8)

3

trans-[Pt{Mo(CO)$_3$Cp}$_2$(PhCN)$_2$] provides an entry into tri- and tetranuclear complexes containing phosphido and sometimes hydrido ligands as well. These results have been compared with those obtained previously with the slightly less reactive ligand PCy$_2$H.[2a] The nature of the R groups influences not only the reactivity of the P–H bond of secondary phosphines but also the chemical behavior of polynuclear complexes containing μ-PR$_2$ bridges. The versatility of our linear trinuclear precursor complexes is also examined with their palladium analogues *trans*-[Pd{M(CO)$_3$Cp}$_2$(PhCN)$_2$] (M = Mo, W) and *trans*-[Pd{Mn(CO)$_5$}$_2$(PhCN)$_2$].[27] Interestingly, we have recently found that the tungsten analogue of 1 can be prepared in good yields by using as synthetic strategy the addition of the corresponding metallophosphine to a Pt(0) complex.[28] An alternative synthesis of the dihydrido, bent-chain complex [(Cp′)MoPt(H)(μ-PPh$_2$)$_2$(CO)$_2$]$_2$ (7) consists of the reaction of the bis(phosphido) complex [PtCl(μ-PPh$_2$)(PPh$_2$H)]$_2$ with 2 equiv [Mo(CO)$_3$Cp′]$^-$. The scope of this method is currently under investigation.

Acknowledgment. The CNRS (Paris), CNR (Rome), and the "Commission of the European Communities" (Contract No. ST2J-0347-C) are gratefully acknowledged for financial support, and Johnson-Matthey Co. Ltd. is acknowledged for a generous loan of PtCl$_2$.

Registry No. 1, 122700-75-8; 1·$^1/_2$PhMe, 122700-85-0; **2a**, 122700-76-9; **2b**, 122700-80-5; **2c**, 122700-81-6; **3**, 122700-77-0; **7a**, 122700-78-1; **7b**, 122723-95-9; **7c**, 122700-82-7; **8**, 122622-59-7; **9**, 122700-79-2; *cis*-**10b**, 122795-90-8; *trans*-**10b**, 122795-91-9; *trans*-[Pt{Mo(CO)$_3$Cp}$_2$(PhCN)$_2$], 83704-68-1; [PtCl(μ-PPh$_2$)(PPh$_2$H)]$_2$, 50771-22-7; Na[Mo(CO)$_3$Cp′], 82661-50-5; Na[W(CO)$_3$Cp], 12107-36-7; *cis*-[PtCl$_2$(PCy$_2$H)$_2$], 122700-83-8; PCy$_2$H, 829-84-5; PtCl$_2$(PhCN)$_2$, 14873-63-3.

Supplementary Material Available: Tables of hydrogen atom coordinates of 1 (Table SI) and anisotropic thermal parameters for non-hydrogen atoms of 1 (Table SII) and 2 (Table SIII) (4 pages); listings of observed and calculated structure factors from the final cycle of least-squares refinement for 1 (Table SIV) and 2 (Table SV) (63 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of Metalated and Cyclometalated Platinum(II) and Platinum(IV) Complexes of β-Diesters[1a]

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Received April 14, 1989

The syntheses and characterization, via ^{1}H and ^{13}C NMR spectroscopy and X-ray crystallography, of several new *C*-malonato Pt(II) and Pt(IV) complexes are described. Cis acyclic bis complexes of C-metalated dimethyl malonate [e.g. Pt(phen)(C$_5$H$_7$O$_4$)$_2$], potential anti-tumor agents, were found to react with X$_2$ *and* CuX$_2$ (X = Cl, Br) to give the corresponding oxidized products but did not react with acyl halides or methyl vinyl ketone. Two new trans cyclometalated Pt(II) complexes, having 5- and 6-membered C,N-chelates, and a novel cyclometalated bridged acetate dimer were characterized by X-ray crystallography. C$_{22}$H$_{24}$N$_2$O$_8$Pt: a = 9.590 (2) Å, b = 29.594 (7) Å, c = 8.442 (2) Å, β = 106.02 (2)°, monoclinic, $P2_1/c$, Z = 4. C$_{24}$H$_{28}$N$_2$O$_8$Pt: a = 10.0905 (12) Å, b = 23.555 (2) Å, c = 10.823 (3) Å, β = 106.23 (2)°, monoclinic, $P2_1/n$, Z = 4. C$_{26}$H$_{30}$N$_2$O$_{12}$Pt$_2$: a = 10.446 (5) Å, b = 16.669 (3) Å, c = 17.038 (3) Å, β = 97.19 (3)°, monoclinic, $P2_1/n$, Z = 4.

Introduction

Monoanions of β-diketones [e.g. 2,4-pentanedione (acac), 1-phenyl-1,3-butanedione (bzac), and 4,6-nonanedione] and β-ketoesters [e.g. ethyl acetoacetate (etac)] form complexes with diverse metals via a resonance stabilized six-membered O,O′-chelate 1.[2] Although this is the most important mode of complexation, other types of complexation are known including O-unidentate, η-allylic, terminal-C, and central-C bonding.[2c] The last of these, central C-bonding

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[1] (a) Chemistry of Heterocyclic Compounds Series. 138. For part 139 see: Baker, G. R.; Fronczek, F. R.; Keifer, G. E.; Marston, C. R.; Modenbach, C. L.; Newkome, G. R.; Puckett, W. E.; Watkins, S. F. *Acta Crystallogr.* 1980, *C44*, 1668. (b) Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803 USA. (c) Undergraduate researcher.

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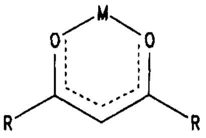
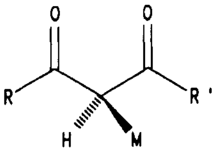
2, is the second most prolific mode of complexation of β-dicarbonyls outnumbered only by O,O′-chelates. Examples of central-C-bonded β-diketone or β-ketoester ligands are known for transition metals with d^6, d^8, and d^{10} configurations including Rh(III), Ir(III), Pt(IV), Rh(I), Pd(II), Pt(II), Au(III), Ag(I), Au(I), and Hg(II),[2] with most of the reports being done on Pd(II), Pt(II), and Pt(IV).



1



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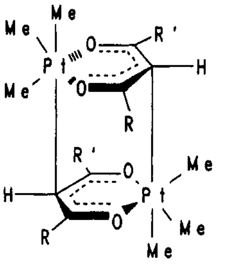
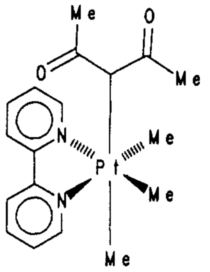


3a $R = R' = C_3H_7$

3b $R = Me$; $R' = OEt$

3c $R = R' = OMe$

3d $R = R' = OEt$



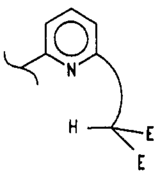
4

The existence of central C-bonded β-dicrbonyls was confirmed in 1960–1962 by Truter et al. through X-ray crystal structure determinations of $[Me_3Pt(C_3H_7COCHCOC_3H_7)]_2$[3] (**3a**), $[Me_3Pt(etac)]_2$[4] (**3b**), and $Me_3Pt(acac\text{-}C^3)(bpy)$[5,6] (**4**). In dimers **3**, the β-dicarbonyls function as terdentate bridging ligands forming both a Pt–C bond and an O,O′-chelate; however, the β-dicarbonyl in **4** is unidentate bonded solely through the central carbon.

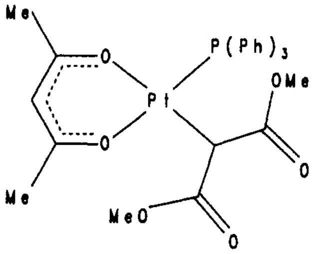
Although there is a plethora of complexes of β–diketone and β–ketoester ligands, there is one type of β-dicarbonyl that has been virtually ignored in this area: β–diesters [i.e. dimethyl (dmmH) and diethyl (demH) malonate esters]. The two main types of bonding known for monoanions of β-diester ligands are central C-bonded and O,O′-chelated. For example, unsubstituted and monosubstituted dialkyl malonates have been shown to form O,O′-chelates with Ti(IV),[7,8] Cr(III),[9] Fe(III),[10] Co(II),[11] Cu(II),[11] Rh(I),[12] Pd(II),[13] Ni(II),[14-16] Pt(IV),[17] Cu(I),[18] U(IV),[19] and Zn(II),[20,21] the last of which behave like Grignard reagents in terms of synthesis, stability, reactivity, etc. The IR carbonyl absorptions of these complexes are characteristic, in that they occur at longer wavelengths than the free malonate which is typical in O,O′-chelated β-dicarbonyl complexes.

Simple dialkyl malonates also from C-bonded complexes with Cu(I),[22] Pt(II),[23] Co(II),[24,25] Pd(II),[26-30] and Fe(II),[31] all of which have IR carbonyl absorption near those of the corresponding non-metalated malonate.

We recently reported a new approach to the synthesis of stable C-bonded β-diester complexes[32] by incorporation of both a dialkyl malonato moiety and a pyridine ring into one ligand (**5**), thereby taking advantage of added stabilization through N,C-chelation. Systems have been designed which facilitate both cis and trans carbon–metal bonds as well as fused bi- and tricyclic complexes.[33-38]



5 $E = CO_2R$



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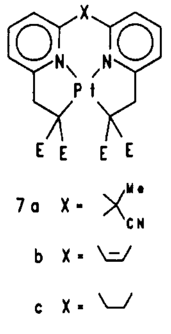
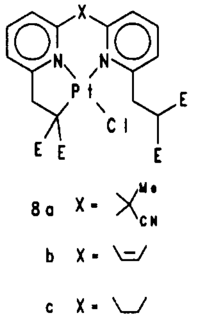
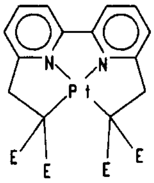
Prior to our initial work, there was only example in the literature of an unsubstituted malonato ligand C-bonded to Pt(II) (**6**),[23] and the only Pt(IV) complexes, which incorporated a C-malonato ligand, were **3c** and **3d** in which the malonate acted as a terdentate ligand giving C-bonded and O,O′-chelation.[17] We recently reported[38] the synthesis of several new cyclometalated complexes of Pt(II) (**7** and **8**) which are C,N,N′,C′- and C,N,N′-chelates, respectively.

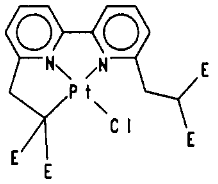


E = CO$_2$Me





7d



8d

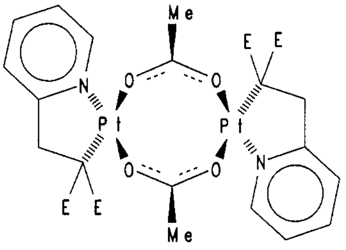
We have recently described[32,39] the anti-tumor activity of some cis-(*C*-malonato)palladium(II) complexes, and thus our interest in platinum is a consequence of this finding coupled with the known anti-tumor activity observed in cis-diammineplatinum complexes,[40] of which cis-diamminedichloroplatinum(II) ("cisplatin") is best known.

The generally accepted mechanism for cisplatin's activity is initial preferential binding at the N(7) position of the guanine moiety of DNA,[41] replacing the chloride ligands, thereby forming inter-[42] and intrastrand[43] cross-links which are the sites of nicking in the DNA. Cisplatin is rather nonselective in that it binds both tumor and normal DNA. The lack of selectivity is generally associated with the lability of the Pt–Cl bond. It was rationalized that complexes in which the non-ammine ligands are not as labile as chloride but yet react with specific sites should lead to more selective anti-tumor activity than cisplatin. To this end, the cis complexes reported herein, which contain platinum–*C*-malonato bonds are prime candidates for anti-tumor activity, especially Pt(phen)(dmm)$_2$ (**16**) which, in addition to the possibility of Pt binding to DNA, also contains a phenanthroline ligand that can intercalate into DNA itself,[44] thereby facilitating the complex's binding to DNA.

In order to compare the similarities and differences of palladium and platinum *C*-malonato complexes, the platinum analogues of previously reported *C*-malonato complexes of two types, cyclometalated complexes **10**[35,36] and the acyclic metalated complexes **15** and **16**,[30] were prepared.

Results

Because of the rapid aquation (hydrolysis) of platinum salts,[45] the initial 2:1 adducts **9** were elusive; alkaline aqueous conditions gave mixtures, presumably of both cis and trans isomers as well as aquated complexes. Despite these complex mixtures, the interesting acetate dimer **11**, whose structure was proven by X-ray crystal diffraction, was isolated from a reaction of K$_2$PtCl$_4$ with methyl (α-methoxycarbonyl)[pyridinyl]-2-propanoate in an acetone/H$_2$O mixture utilizing KOH, as base. Since no acetate was added to the reaction, it was assumed that the commercially obtained K$_2$PtCl$_4$ contained acetate as an impurity. Attempts to prepare **11** under controlled conditions as well as those to reproduce the initial preparation failed. Dimer **11** is the first example in which a ligand of this kind was found to form a dimeric species; even in equimolar ratios, these ligands generally react to form 2:1 complexes.



11

Although reactions using K$_2$PtCl$_4$ and the appropriate ligand in DMF and CH$_3$CN did not give the desired **9**, dichloroplatinum(II) did react with the pyridine ligands in THF at 70 °C to give **9**; however, this reaction depended on the particular lot of PtCl$_2$ used. In an effort to increase the solubility of PtCl$_2$, refluxing dioxane was used as solvent for this reaction with reproducible results being obtained, regardless of the lot of PtCl$_2$ used.

Initial attempts to make **10** using previously reported conditions (K$_2$CO$_3$, DMF, 25 °C) failed. The most obvious variable was the reaction temperature, but even at 50 °C, no reaction occurred. Finally, at 90 °C, cyclometalation succeeded to give **10a** and **10b** in 84% and 19% yields, respectively. The low yield of **10b** was attributed to β-elimination of the cyclometalated complex at the elevated temperatures as shown by the appearance of vinyl absorptions in the ^{1}H NMR spectrum of the crude mixture.

The adducts Pt(bpy)Cl$_2$ (**12**), Pt(phen)Cl$_2$ (**13**), and Pt(diox)Cl$_2$ (diox = 1,1-bis(2-pyridinyl)-1,3-dioxolane) (**14**) were prepared by a modified procedure of Rosenblatt and Schleede[46] where acetone solutions of the ligands were added to an aqueous solution of K$_2$PtCl$_4$ from which the

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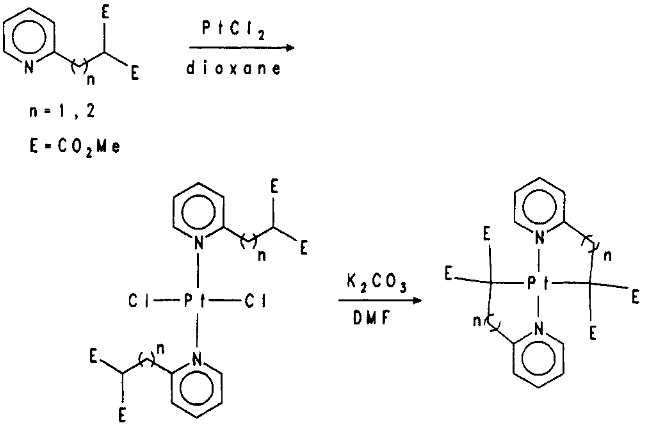
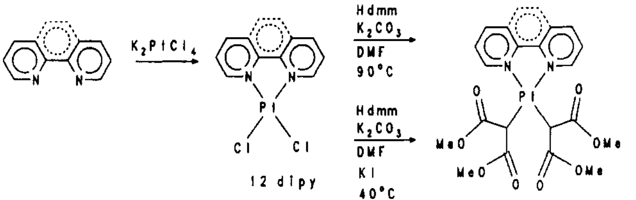


9a n = 1
b n = 2

10a n = 1
b n = 2

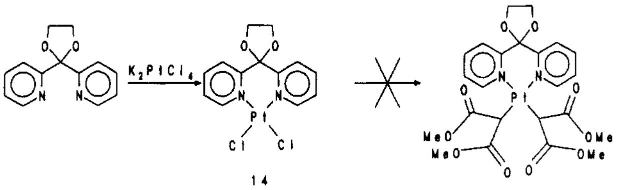
product precipitated. Elevated temperatures (90 °C) were again required for metalation; **15** and **16** were obtained in 78% and 76% yields, respectively. Under these strenuous conditions, it was apparent that dimethyl malonate had self-condensed to give a small amount of a thick oil that was easily removed by chromatography. Pt(diox)Cl$_2$ did not react under any of our conditions.

Presumably the metalations require high temperatures due to the insolubility of the Pt(L)Cl$_2$ adducts in DMF. To circumvent this problem, KI was added to the metalation reactions to generate Pt(L)I$_2$ in situ which, if not more soluble, would certainly be more reactive. An initial test reaction using Pt(phen)Cl$_2$ (**13**), Hdmm, K$_2$CO$_3$, and KI in DMF at 25 °C indeed gave (63%) Pt(phen)(dmm)$_2$ (**16**) along with some mono- and unsubstituted products; raising the temperature to 40 °C improved the yield of **16** to 80%. The complex Pt(bpy)Cl$_2$ (**12**), under identical conditions, gave (74%) Pt(bpy)(dmm)$_2$ (**15**); however, Pt(diox)Cl$_2$ afforded a mixture from which no pure complexes were isolable. Unfortunately, attempts using KI to effect cyclometalation on **9** at lower temperatures (≈40 °C) failed.



12 dipy
13 phen

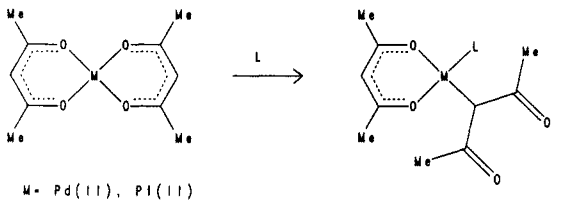
15 dipy
16 phen



14

Simple alkyl organoplatinum(II) complexes are known to react with numerous organic substrates such as alkyl and acyl halides, as well as olefins;[47] however, Pt(phen)(dmm)$_2$ (**16**) failed to react with methyl vinyl ketone, acetyl chloride, or benzoyl chloride, in which each returned the unchanged complex. Reaction of **16** with MeI gave a complex mixture which included Pt(phen)I$_2$ (by two consecutive oxidative addition/reductive elimination sequences whereby dimethyl methylmalonate should also be formed).

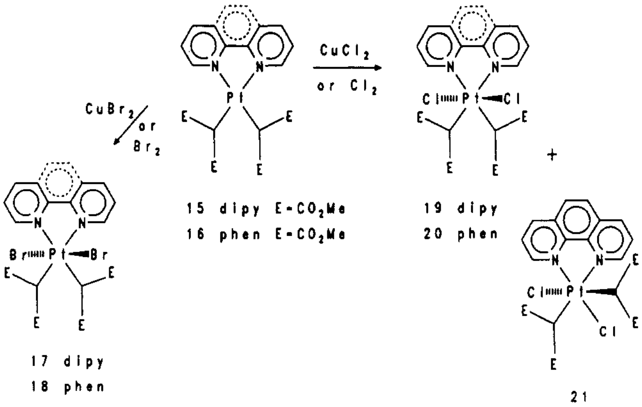
Scheme I



24 L = Me$_2$NH, Et$_2$NH, NH(CH$_3$)CH$_2$Ph
py, 2-, 3-, 4-picoline
PEt$_3$, PMePh$_2$, PPh$_3$, P(Cy)$_3$

Organoplatinum(II) complexes are also known[47] to undergo ligand–ligand exchange, for example, the transfer of a *C*-malonato ligand. However, attempts to react **13** with **16** to obtain Pt(phen)(dmm)Cl gave only starting complexes.

Oxidation of organoplatinum(II) complexes can be accomplished by using X$_2$, and accordingly, when Br$_2$ was added to either Pt(bpy)(dmm)$_2$ (**15**) or Pt(phen)(dmm)$_2$ (**16**), the corresponding Pt(bpy)(dmm)$_2$Br$_2$ (**17**) or Pt(phen)(dmm)$_2$Br$_2$ (**18**), respectively, was immediately formed, both in 98% yield. Predominant trans addition occurred[48] as determined by symmetry in the ^{1}H and ^{13}C NMR spectra of the Pt(IV) complexes. Use of Cl$_2$ effected oxidation of **15** and **16**; lower yields were realized due to over oxidation. Interestingly, the oxidation could be conducted by using CuCl$_2$ (**19–21**) or CuBr$_2$ (**17** and **18**) as the oxidant; in general the yields were lower (70–90%) than with Br$_2$ but higher than with Cl$_2$. Although CuX$_2$ reacts with organometallic complexes by cleaving the carbon–metal bond,[49] Terheijden has recently reported[50] the oxidation of platinum(II) complexes with CuX$_2$ and reported lower yields than with X$_2$. One byproduct isolated from the reaction of Pt(phen)(dmm)$_2$ (**16**) with CuCl$_2$ was the cis addition product giving (5%) the unsymmetric *cis*-dichloro-cis-(dimethyl malonato-*C*)(1,10-phenanthroline)platinum(IV) (**21**). Pt(bpy)(dmm)$_2$ (**15**) gave much cleaner reactions with CuX$_2$ than did Pt(phen)(dmm)$_2$ (**16**).



15 dipy E = CO$_2$Me
16 phen E = CO$_2$Me

19 dipy
20 phen

17 dipy
18 phen

21

Attempts to react **18** with excess Hdmm to form the Pt(IV) complex Pt(phen)(dmm)$_4$ (**22**), which contains four *C*-malonato ligands, gave instead the reduced product Pt(phen)(dmm)$_2$ (**16**). Complex **22** was probably formed

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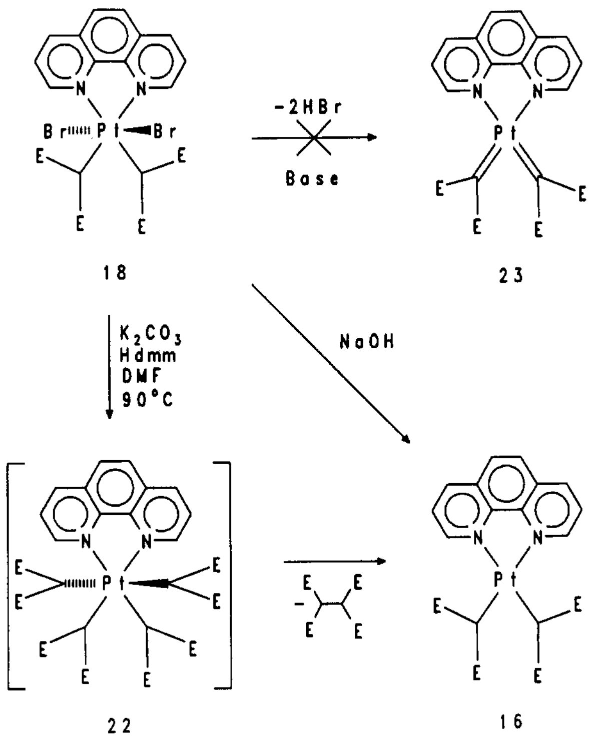
[47] Hartley, F. R. *Compr. Organomet. Chem.* **1982**, *6*, 471–762.

[48] Halpern, J. *Acc. Chem. Res.* **1970**, *3*, 386.

[49] (a) Kochi, J. K. *Organometallic Mechanisms and Catalysis*, Academic: New York, 1978; pp 548–551. (b) Rogers, W. N.; Page, J. A.; Baird, M. C. *Inorg. Chem.* **1981**, *20*, 3521.

[50] (a) Terheijden, J. Ph.D. Thesis, University of Amsterdam, 1986. (b) Terheijden, J.; van Koten, G.; de Booys, J. L.; Ubbels, H. J. C., Stam, C. H. *Organometallics* **1983**, *2*, 83.

in the reaction but was too unstable and underwent reductive elimination of dimethyl 2,3-bis(methoxycarbonyl)butanedioate to give (77%) the reduced complex **16**.



The Pt(IV) complex **18** possesses two acidic protons, and upon treatment with base and elimination of 2 equivs of HBr, the bis(carbene) complex **23** (or its polynuclear equivalent) was expected to form; however, treatment of **18** with NaOH gave (25%) Pt(phen)(dmm)$_2$ with loss of HOBr and Br$^-$. The other possible mechanism that could explain this product is reductive elimination of Br$_2$; however, this is unlikely due to the greater propensity for alkyl–alkyl elimination as opposed to Br$_2$ elimination. Upon workup, the mixture rapidly turned green, an indication of the decomposing intermediate **23**.

Discussion

Kawaguchi[2c] has suggested that the formation of C-bonded versus O,O′-chelated complexes of β-dicarbonyls is directly related to the extent of keto–enol tautomerization of the free β-dicarbonyl; thus low keto:enol ratios favor O,O′-chelation, whereas high ratios favor C-bonded complexes. Unsubstituted malonates have a high "keto:enol" ratio and thus would be expected to form mainly C-bonded complexes. Despite this fact, there are as many literature reports of O,O′-chelated complexes of simple malonates[7–21] as there are of C-bonded complexes;[22–31] however, there are not many examples of either type.

The fact that malonates form both O,O′-chelates and central C-bonded complexes is due to a combination of two counter effects: (1) high keto:enol ratios disfavor O,O′-chelation, whereas (2) chelate stabilization favors O,O′-chelation. These two effects are apparently of approximately equal magnitude, and thus, when a system is sufficiently stable that chelation is not required, C-bonding takes place; however, where extra stabilization is needed, it is available through the O,O′-bonding mode. The stability of a complex is related to the electropositivity of the metal, and thus, early transition metals would be expected to form O,O′-chelates more readily than C-bonded complexes.

The stability of the system is, of course, dependent on the other ligands. An interesting example of this can be seen in the β-diketone systems M(acac)$_2$L (**24**), which are prepared from the bis(chelates) M(acac)$_2$[51] (Scheme I). In the absence of stabilizing ligands, the needed stabilization of chelation in M(acac)$_2$ prohibits C-bonding; however, when good donor ligands are added, C-bonding can occur.

Characterization. One of the most important features about the ^{1}H and ^{13}C NMR spectra of platinum complexes is the fact that, of the six stable isotopes of platinum, only one isotope, namely ^{195}Pt, has a nuclear spin ($^1/_2$). It has a high natural abundance (33.8%) and gyromagnetic ratio ($\gamma = 5.7412$) allowing the ^{195}Pt–C couplings to be easily observed. As with H–H or C–H coupling constants, the ^{195}Pt–H and ^{195}Pt–C coupling constants decrease in magnitude as the distance (number of bonds) between the nuclei increases. Thus for a malonato ligand, the magnitude of the ^{195}Pt–C(2) and ^{195}Pt–CH coupling constants can be used to ascertain if O,O′-chelation or C-bonding occurred.

The coupling constants J_{PtX} can be either positive or negative. However in this work only the absolute values of the coupling constants are reported.

^{1}H NMR Spectroscopy. In the spectrum of the complexes containing Pt–C-malonato bonds, the most important features are the malonato C*H* chemical shifts and ^2J (^{195}Pt–H) coupling constants. Upon metalation, the remaining proton on malonate shifted *downfield* relative to unsubstituted malonate (3.39 ppm) with a range of 4.68–5.38 ppm. Although bordering the vinyl region expected for an O,O′-chelate, the effect is rather a downfield shift resulting from increased C-substitution.

The data that best supported C-bonding of the malonate ligand are the PtCH coupling constants that are only possible in the N,N′-chelates. For the complexes reported here, the range for $^2J_{\mathrm{PtH}}$ is 125.9–129.9 Hz. This coupling constant is too large for an O,O′-chelate having a four-bond coupling constant. Interestingly, the $^2J_{\mathrm{PtH}}$ coupling constant in various methylplatinum complexes ranges from −50 to −85 Hz,[47] which is much lower than those observed here. The only other Pt(II)–*C*-malonato complex reported was Pt(acac)(dmm-C)(PPh$_3$)[23] which had a $^2J_{\mathrm{PtH}}$ coupling constant of 96 Hz.

Although complex **10a** showed symmetry in its NMR spectra, complex **10b** was clearly less symmetric in that two different methoxy protons were seen in the ^{1}H NMR spectrum with one having a large upfield shift (δ 2.83). Also, in the ^{13}C NMR, in addition to two methoxy carbons (δ 49.7, 50.6), two carbonyl resonances were observed (δ 174.5, 176.5). This will be discussed further in the X-ray discussion.

Although in most of the Pt complexes' ^{1}H NMR spectra, the shifts are similar to the corresponding Pd complexes, the MC*H* chemical shifts are significantly different. For the N,N′-chelates, they shift *downfield* compared to the PdC*H* shifts [M(phen)(dmm)$_2$: Pd, 4.25 ppm;[30] Pt = 4.81 ppm; M(bpy)(dmm)$_2$: Pd, 4.12 ppm;[30] Pt, 4.68 ppm; an average *downfield* shift of 0.56 ppm].

The most significant aspect of the ^{1}H NMR spectra of the Pt(IV) complexes is the fact that ^{195}Pt–H coupling

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(51) (a) Ito, T.; Kiriyama, T.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3250. (b) Ito, T.; Kiriyama, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3257. (c) Baba, S.; Ogura, T.; Kawaguchi, S. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 1195. (d) Baba, S.; Ogura, T.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 665. (e) Okeya, S.; Nakamura, Y.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3396. (f) Sahu, B. K.; Mohapatra, B. K. *J. Indian Chem. Soc.* **1981**, *58*, 731. (g) Okeya, S.; Sazaki, H.; Ogita, M.; Takemoto, T.; Onuki, Y.; Nakamura, Y.; Mohapatra, B. K.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1978. (h) Sahu, B. K.; Mohapatra, B. K. *J. Indian Chem. Soc.* **1982**, *59*, 732.

Table I. ^{13}C NMR Spectra of the *C*-Malonato Platinum Complexes [ppm (J_{PtC}, Hz)]

complex	*C*2	*C*3	*C*4	*C*5	*C*6	*C*4a	*C*10a	*C*O	CH_3	Pt*C*(CH)	other
9a	159.6	127.7	139.3	124.3	153.8			168.9	52.8	49.9	37.0 (CH_2)
9b	163.0	126.0	139.1	123.3	153.7			169.5	52.3	50.5	36.0 (α-CH_2) 27.7 (β-CH_2)
10a	172.7 (37.5)	120.7 (33.8)	137.4 (8.7)	121.5 (42.0)	151.8 (30.5)			174.6 (47.9)	50.8	49.3 (453.2)	44.1 (CH_2)
10b	163.3 (10.4)	122.0 (49.9)	137.2 (9.2)	122.5 (26.4)	152.3			174.5 (56.3) 176.5 (63.9)	49.7, 50.6	41.4 (448.0)	41.8 (α-CH_2) 28.9 (β-CH_2)
15	157.0	122.5 (18.2)	139.9 (6.5)	127.6 (27.9)	153.8 (32.2)			177.0	51.5	19.7 (635)	
16	152.9 (34)	125.4 (29)	137.5	126.9		129.6	147.0	176.2 (64)	50.7	18.8 (634)	
17	157.7 (16.1)	123.1 (12.1)	140.2	127.1 (18.1)	155.9 (14.5)			174.3 (43.0)	50.8	21.0 (556.7)	
18	156.0 (15.0)	126.4 (18.6)	139.0	127.5		131.0	146.0	174.5 (44.3)	50.8	21.1 (560)	
19	155.2	123.0 (12.2)	140.2	127.1 (18.0)	156.0 (14.3)			174.4	50.9	21.0 (556.5)	
20	155.5 (14.0)	125.9 (18.3)	139.1	127.5		131.0		173.8	50.9	23.9 (560.6)	

constants are generally about 30% less than corresponding Pt(II) complexes[47] due to decreased electron density on the Pt(IV) atom. In these Pt(IV) complexes the average $^nJ_{PtH}$ values are $^2J = 89.5$ Hz and $^3J = 14.2$ Hz, with an average decrease of 67% supporting the proposed Pt(IV) structures.

Another interesting trend is that the PtC*H* shifts *downfield* by an average of 0.26 ppm for the symmetrical Pt(IV) complexes. The $^2J_{PtH}$ coupling constants for the these complexes range from 84.7 to 98.9 Hz, confirming the fact that C-bonding is maintained during oxidation. The average decrease in $^2J_{PtH}$ as compared with the Pt(II) complexes is 30% as expected for Pt(IV) complexes.[47]

The structure of the unsymmetrical *cis*-dichloro-*cis*-(dimethyl malonato-*C*)(1,10-phenanthroline)platinum(IV) (**21**) was assigned on the basis of its ^1H NMR spectrum which has four different methoxy peaks ranging from δ 2.56 to δ 3.84. The fact that four signals rather than two averaged signals were observed indicates hindered rotation (on the NMR time scale) about the Pt–C bond in this complex, due to a malonate–malonate steric interaction. In addition, the phenanthroline moiety showed two ortho proton signals (δ 10.60 and 10.87; $^3J_{PtH} = 20.0$ and 30.5 Hz, respectively).

^{13}C NMR Spectroscopy. ^{13}C NMR spectral data are presented in Table I. The first thing that is apparent in the ^{13}C NMR spectra of the complexes is the enhanced ^{195}Pt coupling over that seen in the ^1H NMR spectra. The pyridine/bipyridine complexes show a $^4J_{PtC}$ coupling to C-4 of the ring ranging from 6.5 to 9.7 Hz. Two different ^3J coupling constants are possible: C-3 and C-5. Of the two, the phenanthroline complex only showed a coupling in C-3: $^3J_{PtC} = 29.0$ Hz. On first inspection both of these coupling constants would be expected to be similar; however, in these pyridine/dipyridine complexes, C-5 has a larger coupling constant than does C-3. For the 5-membered chelated pyridine/bipyridine complexes, $\Delta(^3J)$ ($J_{C5} - J_{C3}$) range is 7.8–9.7 Hz, very close to the ^4J range (6.5–9.7 Hz), suggesting that for C-5 there is only one pathway for coupling: Pt–N–C(6)–C(5). But for C-3 there are two pathways for coupling: Pt–N–C(2)–C(3) and Pt–N′–C-(2′)–C(2)–C(3) [Pt-β-C-α-C–C(2)–C(3) for **10a**], a *four*-bond route. With the assumption that these four-bond and three-bond coupling constants are of opposite sign and are additive, then the observed coupling constants for C-3 are the expected ones. Sarneski et al. have recently proposed[52] additive multipath couplings such as this between platinum and carbon in small ring systems.

In complex **10b**, ^3J for C-5 is *larger* than for C-3 and $\Delta(^3J)$ is even greater (23.5 Hz). In this case there exists a three-bond and a five-bond path for ^{195}Pt coupling to C-3. With the assumption that the signs for these two constants are the same, then the sum of the two paths gives the larger observed coupling constant.

In complex **10a**, the α-pyridyl carbon showed a two-bond (or a two- and a three-bond) coupling to ^{195}Pt of 17.4 Hz; substantially less than the two-bond coupling constants to C-2 and C-6 (37.5 and 30.5, respectively); however, in **10b**, the corresponding three-bond (or two three-bond paths) coupling constant to the α-pyridyl carbon was 132.0 and the β-carbon has an aggregate four-bond and two-bond coupling constant of 43.5 Hz. The differences seen here are an effect of the 6-membered ring conformation and Karplus effects. The four-bond coupling for the β-carbon is negligible due to the bond angles, whereas the two three-bond paths both have a torsion angle of nearly zero (see X-ray discussion), thereby maximizing the Karplus effect. This result again supports the theory of multipath additive coupling constants.[52]

Of course the largest coupling constants are the one-bond Pt–C ones that can be grouped into two ranges: cyclometalated complexes (448.0–453.2 Hz) and the acyclic cis metalated complexes (634–635 Hz). The main effect here is the differing trans effects, but also the noncyclometalated complexes are more flexible and allow maximum Pt–C orbital overlap and, thus, larger coupling constants.

In the N,N′-chelated complexes, the PtC resonances appeared at 18.8 and 19.7 ppm for phenanthroline and bipyridine, respectively, relative to ≈40 ppm for nonmetalated dimethyl malonate. For the C,N-chelated complexes the carbon bonded to the Pt resonated at δ 49.3 and 41.4 for **10a** and 10b, respectively, compared with δ 49.9 and 50.8 for the ligands. This difference in $\Delta\delta$'s between the N,N′- and C,N-chelates is due to different trans effects.

Before a comparison of the MC shifts for Pd(phen)-$(dmm)_2$ and Pd(bpy)$(dmm)_2$ can be made, the literature values[35,36] *must be reassigned* to 25.6 and 25.4 ppm, respectively. A comparison then shows a slight upfield shift (average 6.2 ppm) in the Pt complexes. This upfield shift was also seen in the C,N-chelated complexes with an average shift of 4.2 ppm. All other chemical shifts for the Pt(II) complexes are as expected and very close to the Pd analogues (largest $\Delta\delta = 2.2$ ppm).

In the dibromo complexes the malonate moieties showed carbonyl carbon coupling to ^{195}Pt of 44.3 Hz for Pt(phen)$(dmm)_2Br_2$ and 43.0 Hz for Pt(bpy)$(dmm)_2Br_2$. The largest coupling constants were for ^{195}Pt–C ranging from 556.5 to 560.5 Hz. The average (558.5 Hz) was 88% that of the Pt(II) complexes (634 Hz) substantiating the proposed structure of the oxidation product.

IR Spectroscopy. The C=O stretching frequency in the IR spectrum of a malonato complex is an excellent indicator of the mode of bonding. For C-bonded complexes, this absorption ranges from 1670 to 1730 cm^{-1}, and for O,O′-chelation the range is generally below 1600 cm^{-1}. Thus, as expected, the delocalization which occurs in

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[52] Sarneski, J. E.; Erickson, L. E.; Reilley, C. N. *J. Magn. Reson.* 1980, *37*, 155.

Table II. Crystal Data and Data Collection Parameters for 10a, 10b, and 11

	10a	10b	11
formula	$C_{22}H_{24}N_2O_8Pt$	$C_{24}H_{28}N_2O_8Pt$	$C_{26}H_{30}N_2O_{12}Pt_2$
fw	639.5	667.6	952.7
cryst system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
a, Å	9.590 (2)	10.0905 (12)	10.446 (5)
b, Å	29.594 (7)	23.555 (2)	16.669 (3)
c, Å	8.442 (2)	10.823 (3)	17.038 (3)
β, deg	106.02 (2)	106.23 (2)	97.19 (3)
V, Å^3	2303 (2)	2470 (1)	2943 (3)
d, g cm^{-3}	1.845	1.795	2.150
Z	4	4	4
T, °C	20	25	25
μ(Mo Kα), cm^{-1}	62.0	57.9	96.6
cryst size, mm	0.03 × 0.32 × 0.44	0.20 × 0.36 × 0.48	0.10 × 0.12 × 0.36
color	colorless	colorless	pale yellow
min rel trans, %	41.46	57.93	83.98
2θ limits, deg	$2 < 2\theta < 50$	$2 < 2\theta < 60$	$2 < 2\theta < 50$
scan rates, deg min^{-1}	0.39–4.0	0.91–4.0	0.53–4.0
precision	$I = 50\sigma(I)$	$I = 50\sigma(I)$	$\mathrm{I} = 50\sigma(I)$
max scan time, s	120	120	120
unique data	4032	7186	5175
obs data	2872	5237	3375
criterion	$I > 2\sigma(I)$	$I > 3\sigma(I)$	$\mathrm{I} > 3\sigma(I)$
variables	298	317	379
R	0.036	0.026	0.032
R_w	0.037	0.029	0.030
extinction		1.28 (3) × 10^{-7}	
max residual, e Å^{-3}	0.98	0.91	1.16
comments		isomorphous with Pd analogue	

Table III. Important Bond Distances (Å) for 10a, 10b, and 11

Complex 10a			
Pt-N(1)	2.013 (5)	Pt-C(7)	2.159 (6)
Pt-N(2)	2.021 (5)	Pt-C(18)	2.142 (6)
Complex 10b			
Pt-N(1)	2.013 (3)	Pt-C(8)	2.176 (3)
Pt-N(2)	2.021 (3)	Pt-C(20)	2.159 (3)
Complex 11			
Pt(1)-Pt(2)	3.1179 (5)	Pt(2)-O(1)	2.013 (8)
Pt(1)-O(2)	2.106 (6)	Pt(2)-O(3)	2.112 (6)
Pt(1)-O(4)	2.009 (7)	Pt(2)-N(2)	1.996 (7)
Pt(1)-N(1)	2.034 (7)	Pt(2)-C(22)	2.061 (9)
Pt(1)-C(11)	2.069 (9)		

Table IV. Important Bond Angles (deg) for 10a, 10b, and 11

Complex 10a			
N(1)-Pt-N(2)	178.4 (2)	Pt-C(18)-C(17)	101.3 (4)
Pt-N(2)-C(16)	114.8 (4)	N(1)-Pt-C(7)	80.6 (2)
Pt-C(7)-C(6)	101.6 (4)	N(2)-Pt-C(7)	100.9 (2)
N(1)-Pt-C(18)	98.3 (2)	C(7)-Pt-C(18)	169.6 (2)
N(2)-Pt-C(18)	80.4 (2)	Pt-N(1)-C(5)	115.1 (4)
Complex 10b			
N(1)-Pt-N(2)	172.2 (1)	Pt-N(2)-C(17)	121.1 (2)
N(1)-Pt-C(8)	84.9 (1)	Pt-C(8)-C(7)	110.0 (2)
N(2)-Pt-C(8)	96.8 (1)	N(1)-Pt-C(20)	96.1 (1)
C(8)-Pt-C(20)	169.2 (1)	N(2)-Pt-C(20)	83.7 (1)
Pt-N(1)-C(5)	120.6 (2)	Pt-C(20)-C(19)	108.9 (2)
Complex 11			
Pt(2)-Pt(1)-O(2)	77.9 (2)	Pt(1)-C(11)-C(10)	105.1 (6)
Pt(2)-Pt(1)-O(4)	81.3 (2)	Pt(1)-N(1)-C(9)	115.5 (6)
Pt(2)-Pt(1)-N(1)	101.5 (2)	Pt(1)-Pt(2)-N(2)	104.8 (2)
Pt(2)-Pt(1)-C(11)	110.0 (3)	Pt(1)-Pt(2)-C(22)	110.9 (2)
O(2)-Pt(1)-O(4)	89.1 (3)	O(1)-Pt(2)-O(3)	90.5 (3)
O(2)-Pt(1)-N(1)	94.2 (3)	O(1)-Pt(2)-N(2)	176.1 (3)
O(2)-Pt(1)-C(11)	171.0 (3)	O(1)-Pt(2)-C(22)	95.1 (3)
O(4)-Pt(1)-N(1)	176.0 (3)	O(3)-Pt(2)-N(2)	91.9 (3)
O(4)-Pt(1)-C(11)	96.2 (3)	O(3)-Pt(2)-C(22)	171.8 (3)
N(1)-Pt(1)-C(11)	80.2 (3)	N(2)-Pt(2)-C(22)	82.2 (3)
Pt(1)-Pt(2)-O(1)	78.7 (2)	Pt(2)-C(22)-C(21)	105.4 (6)
Pt(1)-Pt(2)-O(3)	76.1 (2)	Pt(2)-N(2)-C(20)	115.9 (6)

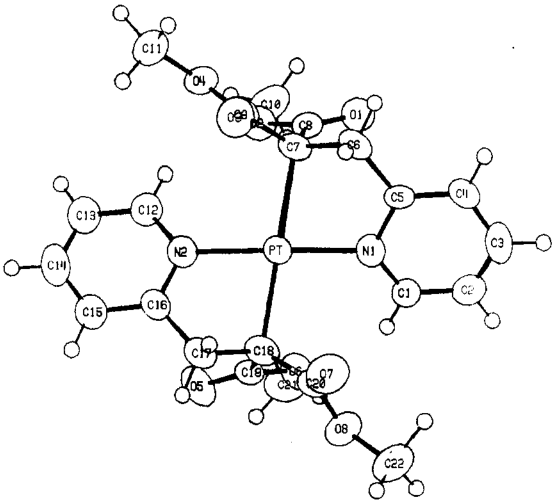

Figure 1. ORTEP drawing of $C_{22}H_{24}N_2O_8Pt$ (**10a**).

O,O′-chelation shifts the carbonyl stretching frequency to longer wavelengths whereas C-bonding has a negligible effect. For these platinum complexes, the C═O stretching absorptions occurred in the range of 1686–1750 cm^{-1} corresponding to the general range for C-bonded malonato complexes.

Structural Characterization of 10a and 10b. To determine the salient structural features in the cyclometalated complexes (**10**), such as Pt–C and Pt–N bond distances and chelate bond angles, single-crystal X-ray structure determinations were undertaken and the crystal data are given in Table II. Important bond distances and angles for **10a** are presented in Tables III and IV, respectively, and an ORTEP drawing is shown in Figure 1. For the 5:5 trans complex **10a**, the Pt-coordination is square-planar with a slight distortion; the ligating atoms are alternately displaced 0.1 Å out of the best plane defined by the four atoms [N(1), N(2), C(7), C(18)]. The Pt atom lies on the line defined by the nitrogen atoms [N(1)–Pt–N(2) = 178.4 (4)°].

The Pt–N bond distances are shorter than those in the Pd(II) analogue[35] [2.040 (3) and 2.042 (3) Å] whereas the Pt–C bond distances are identical with the corresponding distances in the Pd(II) analogue.[35] The chelation angles about Pt [N(1)–Pt–C(7) and N(2)–Pt–C(18)] are 10° less than the 90° square-planar arrangement. Newkome et al. have reported[32] a correlation between the M–C–CH_2 chelate angle and the ^{13}C NMR chemical shift of the central carbon for the Pd(II) complexes; complexes **10** also fit this correlation.

The bond distances and angles in the pyridine rings are all normal. The pyridine rings are planar and form a dihedral angle of 60° with each other and each being ≈30° rotated from the coordination plane in opposite directions. The conformations of both of the five-membered chelate rings are envelopes [Pt–N(1)–C(5)–C(6) = −2.6°; Pt–N(2)–C(16)–C(17) = −0.2°] with the metalated carbons [C(7) and C(18)] forming the flaps, both of which lie on the same face of the coordination plane.

Important bond distances and angles for **10b** are presented in Tables III and IV, respectively, and an ORTEP drawing is shown in Figure 2. The Pt-coordination is square-planar with a slight, but definite, tetrahedral distortion. The platinum atom lies on the best plane defined by the ligating atoms [N(1), N(2), C(8), C(20)] plus platinum with the carbon atoms lying 0.18 Å above the best plane and the nitrogen atoms lying 0.16 Å below it giving

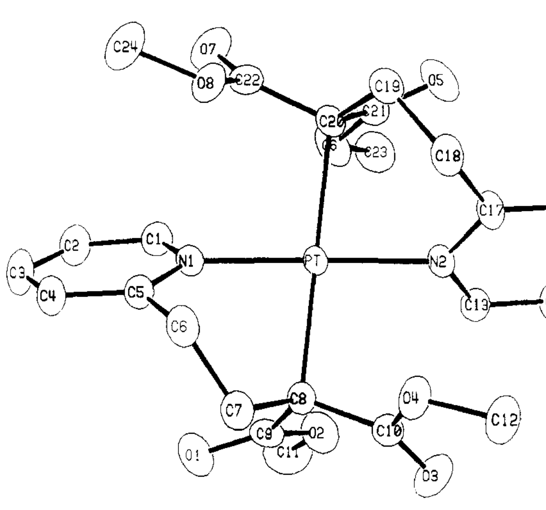

Figure 2. ORTEP drawing of $C_{24}H_{28}N_2O_8Pt$ (**10b**).

the tetrahedral distortion. The N(1)-Pt-N(2) and C(8)-Pt-C(20) angles are 172.2 (1) and 169.2 (1)°, respectively.

The Pt-N bond distances are again shorter than those in the corresponding Pd(II) analogue[35] [2.038 (7) and 2.037 (7) Å]. The Pt-C bond distances are in close agreement with those in the Pd(II) analogue[35] [2.190 (9) and 2.172 (9) Å]. The chelation angles about Pt [N(1)-Pt-C(8) and N(2)-Pt-C(20)] are again less than the expected 90° for a square-planar arrangement [84.9 (1) and 83.7 (1)°, respectively]. The pyridine rings are planar and form a torsion angle of 56.8° with each other; each of the pyridine rings is rotated ca. 61° from the coordination plane.

The 6-membered chelate rings are in "pseudo" boat conformations [Pt-N(1)-C(5)-C(6) = 0.14°; Pt-C(8)-C(7)-C(6) = 12.57°; Pt-N(2)-C(17)-C(18) = 2.93°; Pt-C(20)-C(19)-C(18) = 23.01°] with Pt and C(6) as apexes in one and Pt and C(18) in the other.

The two methoxy groups of each ligand are clearly in different environments with one being over the opposite pyridine ring, thus structurally supporting the large upfield shift observed in the ^1H NMR spectrum (δ 2.83).

The crystal data for complex 11 are given in Table II and important bond distances and angles are presented in Tables III and IV, respectively. Complex 11 is a diacetate bridged dimer with a Pt-Pt distance of 3.1179 (5) Å which is slightly longer (≈0.1 Å) than related structures[53] and far longer than complexes containing a Pt-Pt bond (2.495-2.557 Å).[54] The Pt atoms have square-planar coordination, and the Pt-N bond distances are very close to those in complex **10a**, but the Pt-C distances are slightly shorter. The two pyridyl ligands are arranged in an anti sense in the dimer accounting for the upfield shift of one of the OCH_3 moieties in the ^1H NMR spectrum because of shielding caused by the opposite pyridine ring.[55] The 5-membered chelate rings are in envelope conformations with the metalated carbon being the flap as shown by the torsion angles Pt(1)-N(1)-C(9)-C(10) (0.0°) and Pt(2)-N(2)-C(20)-C(21) (1.1°). The chelate angles are similar to those in **10a**. An ORTEP drawing of **11** is shown in Figure 3.

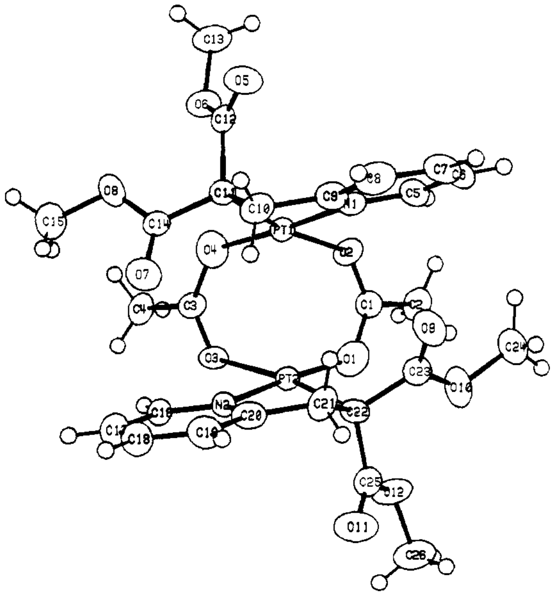

Figure 3. ORTEP drawing of $C_{26}H_{30}N_2O_{12}Pt_2$ (**11**).

Conclusion

Several novel *cis*-organoplatinum(II) complexes have been prepared which incorporate dimethyl malonato-*C* ligands. These complexes were readily oxidized with either Br_2, Cl_2, $CuBr_2$, or $CuCl_2$ to give the corresponding organoplatinum(IV) complexes. In addition, two new trans C,N-cyclometalated platinum(II) complexes were made from 2-pyridyl ligands having dimethyl malonate pendants for metalation. The ^1H and ^{13}C NMR spectra of all complexes were studied and compared to their corresponding Pd(II) complexes.[32] X-ray crystal structures of the cyclometalated complexes proved the presence of trans Pt-C bonding. Anti-tumor activity testing of the cis complexes is presently underway.

Experimental Section

General Comments. All melting points were taken in open capillary tubes with either a Thomas-Hoover Unimelt or a Gallenkamp Melting Point Apparatus and are uncorrected. The ^1H and ^{13}C nuclear magnetic resonance spectra were recorded on a IBM/Bruker NR/80 spectrometer (80.06 and 20.08 MHz, respectively), in $CDCl_3$ solutions, except where noted. Deuterated solvent residues were used as internal standards [$CHCl_3$, 7.27 (^1H) and 77.0 (^{13}C) ppm; Me_2SO, 2.49 (^1H) and 39.5 (^{13}C) ppm], and chemical shift values (δ) are reported in parts per million (ppm) downfield from tetramethylsilane (TMS). Infrared spectra (IR) were recorded on IBM IR/38 Fourier transform infrared spectrophotometer. Elemental analyses were conducted by either Galbraith Laboratories, Inc. (Knoxville, TN) or M-H-W Laboratories (Phoenix, AZ). "Dry column" flash chromatography was performed by the method of Harwood[56] using preparative grade silica gel (Brinkman PF-254-366) and the eluants specified.

Unless otherwise noted, all reagents and solvents utilized were of reagent grade and no further purification was undertaken. Methyl (α-methoxycarbonyl)[pyridine]-2-propanoate[35] and methyl (α-methoxycarbonyl)[pyridine]-2-butanoate[36] were prepared by previously published procedures. Dichloroplatinum(II) and potassium tetrachloroplatinite were obtained from Engelhard Corp.

X-ray. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer equipped with MoKα radiation (λ = 0.71073 Å) and a graphite monochromator, by ω-2θ scans of variable speed designed to yield equal relative precision for all significant data.

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(53) (a) deMeester, P.; Skapski, A. C. *J. Chem. Soc., Dalton Trans.* **1973**, 1194. (b) Cooper, M. K.; Guerney, P. J.; Goodwin, H. J.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1982**, 757.

(54) (a) Carrondo, M. A. A. F. deC. T.; Skapski, A. C. *Acta Crystallogr.* **1978**, *B34*, 3576. (b) Carrondo, M. A. A. F. deC. T.; Skapski, A. C. *Acta Crystallogr.* **1978**, *B34*, 1857. (c) Schagen, J. D.; Overbeek, A. R.; Schenk, H. *Inorg. Chem.* **1978**, *17*, 1938.

(55) ^1H NMR ($CDCl_3$): δ 2.20 (s, O_2CCH_3, 1 H), 2.97 (d, α-CH_2, J = 16.9 Hz, 1 H), 3.15 (s, OCH_3, 3 H), 3.56 (s, OCH_3, 3 H), 3.75 (d, α-CH_2, J = 16.9 Hz, 1 H), 6.96-7.16 (m, 5-pyr*H*, 1 H), 7.47 (d, 3-pyr*H*, $J_{3,4}$ = 7.1 Hz, 1 H), 7.70-7.92 (m, 4-pyr*H*, 1 H), 8.26 (ds,[57] 6-pyr*H*, $J_{5,6}$ = 5.9, J_{PtH} = 30.2 Hz, 1 H).

(56) Harwood, L. M. *Aldrichim. Acta* **1985**, *18*, 25.

Table V. Coordinates for $Pt(C_{11}H_{12}NO_4)_2$ (10a)

atom	*x*	*y*	*z*
Pt	0.41814 (3)	0.12295 (1)	0.25561 (3)
O(1)	0.0834 (7)	0.1716 (2)	−0.0252 (6)
O(2)	0.1341 (6)	0.1001 (2)	−0.0726 (6)
O(3)	0.1470 (7)	0.0771 (2)	0.4210 (6)
O(4)	0.0670 (6)	0.0521 (2)	0.1628 (6)
O(5)	0.7578 (7)	0.0830 (2)	0.1666 (7)
O(6)	0.6926 (6)	0.1540 (2)	0.1089 (6)
O(7)	0.6754 (7)	0.1655 (2)	0.5924 (6)
O(8)	0.7992 (7)	0.1871 (2)	0.4211 (7)
N(1)	0.3887 (7)	0.1902 (2)	0.2607 (7)
N(2)	0.4530 (7)	0.0557 (2)	0.2492 (7)
C(1)	0.4731 (9)	0.2219 (3)	0.2280 (10)
C(2)	0.4455 (10)	0.2666 (3)	0.2358 (11)
C(3)	0.3283 (11)	0.2804 (3)	0.2840 (11)
C(4)	0.2333 (9)	0.2484 (3)	0.3081 (9)
C(5)	0.2619 (8)	0.2035 (2)	0.2934 (8)
C(6)	0.1641 (9)	0.1655 (3)	0.3123 (9)
C(7)	0.1850 (8)	0.1247 (3)	0.2064 (8)
C(8)	0.1265 (8)	0.1344 (3)	0.0294 (9)
C(9)	0.1328 (9)	0.0834 (3)	0.2747 (9)
C(10)	0.0808 (12)	0.1078 (3)	−0.2434 (10)
C(11)	0.0156 (12)	0.0123 (3)	0.2213 (12)
C(12)	0.3713 (10)	0.0258 (3)	0.1473 (9)
C(13)	0.4046 (11)	−0.0182 (3)	0.1461 (11)
C(14)	0.5263 (12)	−0.0340 (3)	0.2533 (12)
C(15)	0.6189 (11)	−0.0038 (3)	0.3555 (11)
C(16)	0.5818 (9)	0.0412 (2)	0.3507 (9)
C(17)	0.6729 (9)	0.0774 (3)	0.4467 (10)
C(18)	0.6496 (8)	0.1219 (3)	0.3504 (8)
C(19)	0.7076 (8)	0.1175 (2)	0.2048 (9)
C(20)	0.7043 (9)	0.1600 (3)	0.4656 (9)
C(21)	0.7319 (11)	0.1498 (3)	−0.0428 (10)
C(22)	0.8545 (13)	0.2237 (3)	0.5343 (13)

A maximum was placed on the time allowed for scanning a single reflection. Crystal data and experimental details are listed in Table II. One quadrant of data was measured for each crystal within the specified angular limits. Data reduction included corrections for background, Lorentz, polarization, and absorption by Ψ scans.

Structures were solved by heavy-atom methods and refined by full-matrix least squares, treating non-hydrogen atoms anisotropically. Hydrogen atoms were located by difference maps and included as fixed contributions. Final *R* factors and residual electron densities are given in Table II; coordinates are listed in Tables V–VII.

Preparation of Adducts 9a and 9b. *trans*-Dichlorobis{methyl (α-methoxycarbonyl)[pyridine]-2-propanoate-*N*}platinum(II) (9a). A stirred mixture of $PtCl_2$ (71 mg, 267 μmol) and methyl (α-methoxycarbonyl)[pyridine]-2-propanoate (123 mg, 552 μmol) in 1,4-dioxane (10 mL) was refluxed for 24 h. After the mixture was cooled, the solvent was removed in vacuo and the resulting solid was extracted with Et_2O to give (70%) adduct **9a**, as a grayish white solid: 133 mg; mp 233–235 °C; ^1H NMR (Me_2SO-d_6) δ 3.74 (s, OCH_3, 6 H), 4.20 (d, CH_2, J = 7.4 Hz, 2 H), 5.12 (t, C*H*, J = 7.4 Hz, 1H), 7.44–7.58 (m, 3,5-pyr*H*, 2 H), 7.93 (m, 4-pyr*H*, 1 H), 8.88 (ds,[57] 6-pyr*H*, $J_{5,6}$ = 5.2 Hz, J_{PtH} = 32.3 Hz, 1 H); IR (KBr) 1732 vs (C═O), 1213 (C—O) cm^{-1}. Anal. Calcd for $C_{22}H_{26}N_2Cl_2O_8Pt$: C, 37.09; H, 3.68; N, 3.93. Found: C, 36.91; H, 3.89; N, 3.79.

***trans*-Dichlorobis{methyl (α-methoxycarbonyl)[pyridine]-2-butanoate-*N*}platinum(II) (9b)** was similarly prepared from methyl (α-methoxycarbonyl)[pyridine]-2-butanoate and $PtCl_2$: 83%; mp 164–167 °C; ^1H NMR (Me_2SO-d_6) δ 2.38–2.67 (m, β-CH_2, 2H), 3.71–3.96 (m, α-CH_2, C*H*, 3 H), 3.74 (s, CH_3, 6 H), 7.35–7.59 (m, 3,5-pyr*H*, 2 H), 7.93 (ddd, 4-pyr*H*, $J_{3,4}$ = $J_{4,5}$ = 6.8, $J_{4,6}$ = 2.0 Hz, 1 H), 9.00 (ds,[57] 6-pyr*H*, $J_{5,6}$ = 5.1, J_{PtH} = 26.4 Hz, 1 H); IR (KBr) 1728 vs (C═O), 1228 (C—O) cm^{-1}. Anal. Calcd for $C_{24}H_{30}N_2Cl_2O_8Pt$: C, 38.93; H, 4.08; N, 3.78. Found: C, 39.07; H, 4.11; N, 3.79.

Table VI. Coordinates for $Pt(C_{12}H_{14}NO_4)_2$ (10b)

atom	*x*	*y*	*z*
Pt	0.18987 (1)	0.12188 (1)	0.18534 (1)
O(1)	−0.0434 (3)	0.2410 (1)	0.1995 (3)
O(2)	0.1063 (3)	0.2497 (1)	0.0829 (3)
O(3)	−0.0061 (4)	0.1846 (1)	−0.1370 (3)
O(4)	−0.0423 (3)	0.0950 (1)	−0.0895 (3)
O(5)	0.5670 (3)	0.0851 (1)	0.2148 (3)
O(6)	0.4965 (3)	0.1538 (1)	0.3225 (3)
O(7)	0.4376 (3)	0.0794 (1)	0.5129 (3)
O(8)	0.2535 (3)	0.0261 (1)	0.4227 (3)
N(1)	0.1301 (3)	0.1399 (1)	0.3435 (3)
N(2)	0.2669 (3)	0.1131 (1)	0.0330 (3)
C(1)	0.2103 (4)	0.1734 (2)	0.4357 (4)
C(2)	0.1695 (5)	0.1915 (2)	0.5398 (4)
C(3)	0.0446 (5)	0.1743 (2)	0.5542 (4)
C(4)	−0.0381 (4)	0.1398 (2)	0.4599 (4)
C(5)	0.0040 (4)	0.1239 (2)	0.3519 (4)
C(6)	−0.0836 (4)	0.0932 (2)	0.2402 (4)
C(7)	−0.1255 (4)	0.1315 (2)	0.1202 (4)
C(8)	−0.0057 (4)	0.1601 (2)	0.0809 (3)
C(9)	0.0126 (4)	0.2204 (2)	0.1253 (4)
C(10)	−0.0178 (4)	0.1504 (2)	−0.0582 (4)
C(11)	0.1427 (6)	0.3047 (2)	0.1379 (6)
C(12)	−0.0454 (5)	0.0800 (2)	−0.2186 (4)
C(13)	0.3031 (4)	0.1601 (2)	−0.0235 (4)
C(14)	0.3682 (5)	0.1569 (2)	−0.1188 (4)
C(15)	0.3965 (5)	0.1039 (2)	−0.1605 (4)
C(16)	0.3596 (5)	0.0563 (2)	−0.1036 (4)
C(17)	0.2977 (4)	0.0616 (2)	−0.0049 (4)
C(18)	0.2652 (4)	0.0126 (2)	0.0673 (4)
C(19)	0.3516 (4)	0.0120 (2)	0.2094 (4)
C(20)	0.3628 (4)	0.0690 (2)	0.2815 (4)
C(21)	0.4871 (4)	0.1013 (2)	0.2714 (4)
C(22)	0.3602 (4)	0.0599 (2)	0.4167 (4)
C(23)	0.5967 (5)	0.1916 (2)	0.2941 (5)
C(24)	0.2382 (6)	0.0152 (2)	0.5473 (5)

Preparation of the C,N-Chelates 10a and 10b. *trans*-Bis{methyl (α-methoxycarbonyl)[pyridine]-2-propanoate-*C*,*N*}platinum(II) (10a). A stirred mixture of **9a** (86 mg, 121 μmol) and excess anhydrous K_2CO_3 in DMF was heated to 90 °C and stirred for 12 h after which the DMF was removed in vacuo. The remaining solid was partially dissolved in $CHCl_3$ and then filtered through Celite. The $CHCl_3$ was removed and the product passed through a short chromatographic column (SiO_2, $CHCl_3$) to give (84%) **10a**, as a yellow solid: 65 mg; mp 205–208 °C dec; ^1H NMR δ 3.45 (s, CH_3, 6 H), 3.66 (ss,[57] CH_2, J_{PtH} = 20.3 Hz, 2 H), 7.15–7.33 (m, 5-pyr*H*, 1 H), 7.53–7.79 (m, 3.4-pyr*H*, 2 H), 9.18 (ds,[57] $J_{5,6}$ = 5.1, J_{PtH} = 36.8 Hz, 1 H); IR (KBr) 1686 vs (C═O), 1181 (C—O) cm^{-1}. Anal. Calcd for $C_{22}H_{24}N_2O_8Pt$: C, 41.32; H, 3.78; N, 4.38. Found: C, 40.98; H, 4.01; N, 4.25.

***trans*-Bis{methyl (α-methoxycarbonyl)[pyridine]-2-butanoate-*C*,*N*}platinum(II) (10b)** was similarly prepared (purification was done by dry-column flash chromatography[56] eluting initially with $CHCl_3$ and then with 50% $CHCl_3$/MeOAc) from **9b**: 19%; mp 220–222 °C dec; ^1H NMR δ 2.12–2.30 (m, α-CH_2, 2 H), 2.83 (s, CH_3, 3 H), 2.93–3.74 (m, β-CH_2, 2 H), 3.29 (s, CH_3, 3 H), 7.06–7.44 (m, 3,5-pyr*H*, 2 H), 7.71 (ddd, 4-pyr*H*, $J_{4,5}$ = $J_{3,4}$ = 7.6, $J_{4,6}$ = 1.7 Hz, 1 H), 8.91 (ddds,[57] 6-pyr*H*, $J_{5,6}$ = 5.8, $J_{4,6}$ = 1.5, $J_{3,6}$ = 0.7, J_{PtH} = 41.2 Hz, 1 H); IR (KBr) 1690 s (C═O), 1196 (C—O) cm^{-1}. Anal. Calcd for $C_{24}H_{28}N_2O_8Pt$: C, 43.19; H, 4.23; N, 4.20. Found: C, 43.32; H, 4.41; N, 4.13.

Preparation of the N,N-Chelated Adducts 12, 13, and 14. Dichloro(2,2′-bipyridine)platinum(II) (12). To a stirred solution of K_2PtCl_4 (960 mg, 2.31 mmol) in H_2O (50 mL) was added 2,2′-bipyridine (377 mg, 2.42 mmol) in acetone (15 mL), and the temperature was maintained at 65 °C for 12 h . The yellow precipitate that formed was then filtered and rinsed with H_2O to give (85%) **12**, as a yellow powder: 829 mg; mp 368–370 °C; ^1H NMR (Me_2SO-d_6) δ 7.83 (dd, 5-pyr*H*, $J_{4,5}$ = 7.8, $J_{5,6}$ = 5.7 Hz, 1 H), 8.34 (d, 3-pyr*H*, $J_{3,4}$ = 8.0 Hz, 1 H), 8.48–8.71 (m, 4-pyr*H*, 1 H), 9.50 (ds,[57] 6-pyr*H*, $J_{5,6}$ = 5.7, J_{PtH} = 40.4 Hz, 1 H); ^{13}C NMR (Me_2SO-d_6 limited solubility) δ 124.2 (C-3, J_{PtC} = 30.6 Hz), 127.7 (C-5, J_{PtC} = 38.4 Hz), 140.5 (C-4, J_{PtC} = 9.7 Hz), 148.5 (C-6, J_{PtC} = 33.3 Hz) (C-2 not observed); IR (KBr) 766, 720 cm^{-1}. Anal. Calcd for $C_{10}H_8N_2Cl_2Pt$: C, 28.46; H, 1.91; N, 6.64. Found: C, 28.37; H, 1.70; N, 6.46.

Dichloro(1,10-phenanthroline)platinum(II) (13) was similarly prepared (86%) from 1,10-phenanthroline monohydrate and

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[57] Satellites due to coupling to ^{195}Pt.

Table VII. Coordinates for $\mathrm{Pt_2C_{26}H_{30}N_2O_{12}}$ (11)

atom	x	y	z	atom	x	y	z
Pt(1)	0.04712 (3)	0.10894 (2)	0.11225 (2)	C(6)	0.0108 (10)	0.0984 (7)	0.3603 (6)
Pt(2)	−0.12984 (3)	0.25434 (2)	0.05785 (2)	C(7)	0.1070 (10)	0.1480 (7)	0.3919 (6)
O(1)	−0.2616 (7)	0.1685 (5)	0.0698 (4)	C(8)	0.1871 (10)	0.1819 (7)	0.3425 (6)
O(2)	−0.1383 (5)	0.0577 (4)	0.1049 (4)	C(9)	0.1632 (8)	0.1669 (6)	0.2628 (5)
O(3)	−0.0887 (6)	0.2021 (4)	−0.0491 (3)	C(10)	0.2437 (9)	0.2015 (6)	0.2022 (6)
O(4)	0.0417 (6)	0.0956 (5)	−0.0053 (4)	C(11)	0.2376 (8)	0.1456 (6)	0.1327 (5)
O(5)	0.3744 (6)	0.0594 (5)	0.2192 (4)	C(12)	0.3120 (8)	0.0664 (6)	0.1554 (5)
O(6)	0.2952 (6)	0.0092 (4)	0.1011 (4)	C(13)	0.3485 (10)	−0.0661 (6)	0.1258 (7)
O(7)	0.2599 (8)	0.2583 (5)	0.0501 (5)	C(14)	0.2777 (8)	0.1882 (6)	0.0621 (5)
O(8)	0.3382 (7)	0.1431 (5)	0.0141 (4)	C(15)	0.3717 (12)	0.1834 (9)	−0.0543 (7)
O(9)	−0.1200 (7)	0.2538 (5)	0.2776 (4)	C(16)	0.0481 (9)	0.3604 (6)	−0.0189 (5)
O(10)	−0.3187 (6)	0.2399 (5)	0.2173 (4)	C(17)	0.1335 (10)	0.4226 (7)	−0.0243 (6)
O(11)	−0.2758 (7)	0.4479 (5)	0.1269 (5)	C(18)	0.1630 (10)	0.4694 (7)	0.0407 (7)
O(12)	−0.3914 (6)	0.3384 (4)	0.0996 (4)	C(19)	0.1064 (10)	0.4575 (7)	0.1105 (6)
N(1)	0.0661 (6)	0.1213 (5)	0.2319 (4)	C(20)	0.0169 (9)	0.3937 (6)	0.1115 (6)
N(2)	−0.0084 (6)	0.3450 (5)	0.0471 (4)	C(21)	−0.0498 (9)	0.3690 (6)	0.1795 (5)
C(1)	−0.2444 (8)	0.0922 (6)	0.0894 (5)	C(22)	−0.1708 (9)	0.3207 (5)	0.1537 (5)
C(2)	−0.3611 (9)	0.0418 (7)	0.0948 (6)	C(23)	−0.1975 (9)	0.2688 (6)	0.2227 (5)
C(3)	−0.0211 (8)	0.1404 (6)	−0.0620 (5)	C(24)	−0.3431 (11)	0.1845 (8)	0.2769 (7)
C(4)	−0.0117 (9)	0.1207 (7)	−0.1473 (5)	C(25)	−0.2817 (9)	0.3767 (6)	0.1273 (5)
C(5)	−0.0094 (9)	0.0864 (6)	0.2793 (6)	C(26)	−0.5042 (10)	0.3875 (7)	0.0852 (7)

$\mathrm{K_2PtCl_4}$: mp 400 °C; ^{1}H NMR ($\mathrm{Me_2SO}$-d_6) δ 8.17 (dd, 3-phen*H*, $J_{3,4}$ = 8.2, $J_{2,3}$ = 5.5 Hz, 1 H), 8.29 (s, 5-phen*H*, 1 H), 9.04 (dd, 4-phen*H*, $J_{3,4}$ = 8.2, $J_{2,4}$ = 1.3 Hz, 1 H), 9.71 (dds,[57] 2-phen*H*, $J_{2,3}$ = 5.5, $J_{2,4}$ = 1.3, J_{PtH} = 41.3 Hz, 1 H); IR (KBr) 839, 708 cm^{-1}. Anal. Calcd for $\mathrm{C_{12}H_8N_2Cl_2Pt}$: C, 32.31; H, 1.81; N, 6.28. Found: C, 32.48; H, 1.80; N, 6.24.

Dichloro[1,1-bis(2-pyridyl)-1,3-dioxolane]platinum(II) (14) was similarly prepared (52%) from 1,1-bis(2-pyridyl)-1,3-dioxolane and $\mathrm{K_2PtCl_4}$: mp 313–315 °C dec; ^{1}H NMR δ 4.25–4.45 (m, C*H*$_2$, 2 H), 7.40 (ddd, 5-pyr*H*, $J_{4,5}$ = 5.9, $J_{5,6}$ = 5.6, $J_{3,5}$ = 3.3 Hz, 1 H), 7.79–8.04 (m, 3,4-pyr*H*, 2 H), 9.37 (ds,[57] 6-pyr*H*, $J_{5,6}$ = 5.6, J_{PtH} = 46.6 Hz, 1 H); IR (KBr) 1090 cm^{-1} (C-O). Anal. Calcd for $\mathrm{C_{13}H_{12}N_2Cl_2O_2Pt}$: C, 31.60; H, 2.45; N, 5.67. Found: C, 31.96; H, 2.17; N, 5.59.

Preparation of the N,N′-Chelated *C*-Malonato Complexes 15 and 16. Bis(dimethyl malonato-*C*)(2,2′-bipyridine)platinum(II) (15). Method A. A stirred mixture of adduct 12 (90 mg, 213 μmol), dimethyl malonate (140 mg, 1.06 mmol), and anhydrous $\mathrm{K_2CO_3}$ (293 mg, 2.13 mmol) was kept at 90 °C for 18 h. The DMF and excess malonate were then removed in vacuo, and the resulting solid was extracted with $\mathrm{CHCl_3}$. After the $\mathrm{CHCl_3}$ was removed, the product was purified on a silica gel column, eluting first with $\mathrm{CHCl_3}$ and then with MeOAc to obtain (78%) 15, as a bright yellow solid.

Method B. A stirred solution of adduct 12 (573 mg, 1.36 mmol) and KI (1.38 g, 8.31 mmol) in DMF (5 mL) was heated to 100 °C for 5 min. After the solution was cooled to 40 °C, dimethyl malonate (895 mg, 6.78 mmol) and anhydrous $\mathrm{K_2CO_3}$ (1.00 g, 5.68 mmol) were added and the mixture was stirred for 24 h at 40 °C. The same workup as in method A above yielded (74%) 15: method A, 102 mg; method B, 617 mg; mp 210–214 °C dec; ^{1}H NMR δ 3.62 (ss,[57] C*H*$_3$, J_{PtH} = 3.0 Hz, 6 H), 4.68 (ss,[57] C*H*, J_{PtH} = 129.4 Hz, 1 H), 7.61 (ddd, 5-pyr*H*, $J_{5,6}$ = $J_{4,5}$ = 6.1, $J_{3,5}$ = 2.8 Hz, 1 H), 7.99–8.19 (m, 3,4-pyr*H*, 2 H), 10.09 (ds,[57] 6-pyr*H*, $J_{5,6}$ = 6.1, J_{PtH} = 25.6 Hz, 1 H); IR (KBr) 1744 vs, 1721 s (C=O), 1136 m (C—O), 783, 729 cm^{-1}. Anal. Calcd for $\mathrm{C_{20}H_{22}N_2O_8Pt}$: C, 39.16; H, 3.62; N, 4.57. Found: C, 38.95; H, 3.75; N, 4.26.

Bis(dimethyl malonato-*C*)(1,10-phenanthroline)platinum(II) (16) was prepared by both methods from 13: method A, 76%; method B, 80%; mp 256–257 °C dec; ^{1}H NMR δ 3.64 (ss,[57] C*H*$_3$, J_{PtH} = 3.4 Hz, 6 H), 4.81 (ss,[57] C*H*, J_{PtH} = 129.9 Hz, 1 H), 7.89 (s, 5-phen*H*, 1 H), 7.93 (dd, 3-phen*H*, $J_{3,4}$ = 8.2, $J_{2,3}$ = 5.4 Hz, 1 H), 8.53 (dd, 4-phen*H*, $J_{2,4}$ = 1.4, $J_{3,4}$ = 8.2 Hz, 1 H), 10.44 (dds,[57] 2-phen*H*, $J_{2,3}$ = 5.4, $J_{2,4}$ = 1.4, J_{PtH} = 25.6 Hz, 1 H); IR (KBr) 1725 vs (C=O), 1138 (C—O), 841, 716 cm^{-1}. Anal. Calcd for $\mathrm{C_{22}H_{22}N_2O_8Pt}$: C, 41.45; H, 3.48; N, 4.39. Found: C, 41.36; H, 3.42; N, 4.22.

Preparation of the Dibromoplatinum(IV) Complexes 17 and 18. *af*-Dibromo-*de*-bis(dimethyl malonato-*C*)-*bc*-(2,2′-bipyridine)platinum(IV) (17). Method A. A 4% solution of bromine in $\mathrm{CHCl_3}$ was added dropwise to a stirred solution of 15 (169 mg, 276 μmol) in $\mathrm{CHCl_3}$ (5 mL) until no further color change was noted (initially the solution got lighter and then suddenly turned dark from excess $\mathrm{Br_2}$). The solvent was then removed in vacuo to give (98%) the oxidized product 17.

Method B. A mixture of cupric bromide (70 mg, 313 μmol) and 15 (49 mg, 80 μmol) in acetone (20 mL) was stirred at 25 °C for 12 h. The acetone was evaporated and the residue redissolved in $\mathrm{CH_2Cl_2}$ which was then filtered to remove Cu salts. Removal of the $\mathrm{CH_2Cl_2}$ in vacuo gave (73%) 17, as a light yellow solid: method A, 209 mg; method B, 46 mg; mp 342–346 °C; ^{1}H NMR δ 3.72 (s, C*H*$_3$, 6 H), 4.94 (ss,[57] C*H*, J_{PtH} = 89.9 Hz, 1 H), 7.59–7.77 (m, 5-pyr-*H*, 1 H), 8.02–8.29 (m, 3,4-pyr*H*, 2 H), 10.53 (ds,[57] 6-pyr*H*, $J_{5,6}$ = 6.6, J_{PtH} = 14.1 Hz); IR (KBr) 1744 vs (C=O), 1127 (C—O), 778, 732 cm^{-1}. Anal. Calcd for $\mathrm{C_{20}H_{22}N_2Br_2O_8Pt}$: C, 31.07; H, 2.87; N, 3.62. Found: C, 31.42; H, 3.21; N, 3.22.

***af*-Dibromo-*de*-bis(dimethyl malonato-*C*)-*bc*-(1,10-phenanthroline)platinum(IV) (18)** was prepared by both methods from 16: method A, 98%; method B, 91%; mp <350 °C; ^{1}H NMR δ 3.76 (ss,[57] C*H*$_3$, J_{PtH} = 3.0 Hz, 6 H), 5.04 (ss,[57] C*H*, J_{PtH} = 90.3 Hz, 1 H), 7.96 (s, 5-phen*H*, 1 H), 8.00 (dd, 3-phen*H*, $J_{3,4}$ = 8.2, $J_{2,3}$ = 5.5 Hz, 1 H), 8.49 (dd, 4-phen*H*, $J_{3,4}$ = 8.2, $J_{2,4}$ = 1.3 Hz, 1 H), 10.89 (dds,[57] 2-phen*H*, $J_{2,3}$ = 5.5, $J_{2,4}$ = 1.3 Hz, J_{PtH} = 15.4 Hz, 1 H); IR (KBr) 1746 s (C=O), 1144 s (C—O), 845, 716 cm^{-1}. Anal. Calcd for $\mathrm{C_{22}H_{22}N_2Br_2O_8Pt}$: C, 33.14; H, 2.78; N, 3.51. Found: C, 33.35; H, 2.48; N, 3.42.

Preparation of the Dichloroplatinum(IV) Complexes 19 and 20. *af*-Dichloro-*de*-bis(dimethyl malonato-*C*)-*bc*-(2,2′-bipyridine)platinium(IV) (19). Method A. A cooled (0 °C) saturated solution of chlorine in $\mathrm{CHCl_3}$ was added dropwise to a cooled (0 °C) stirred solution of 15 (61 mg, 100 μmol) in $\mathrm{CHCl_3}$ until no further color change was noted. (Initially the solution got lighter and then turned darker from excess chlorine.) The excess chlorine and $\mathrm{CHCl_3}$ were then removed in vacuo, and the product was passed through a short silica column eluting with $\mathrm{CHCl_3}$ to give (56%) 19.

Method B. A mixture of 15 (45 mg, 70 μmol) and $\mathrm{CuCl_2}$ (40 mg, 300 μmol) was stirred in acetone (10 mL) at 25 °C for 1 h. After the solution was filtered the acetone was removed, the resulting light yellow solid was purified by using flash-dry chromatography[56] on $\mathrm{SiO_2}$ eluting initially with $\mathrm{CH_2Cl_2}$ and finally with 3% EtOH/$\mathrm{CH_2Cl_2}$ to give (83%) 19, as a light yellow solid: method A, 38 mg; method B, 42 mg; mp >390 °C dec; ^{1}H NMR δ 3.72 (s, C*H*$_3$, 6 H), 4.93 (ss,[57] C*H*, J_{PtH} = 89.1 Hz, 1 H), 7.60–7.78 (m, 5-pyr*H*, 1 H), 7.91–8.18 (m, 3,4-pyr*H*, 2 H), 10.53 (ds,[57] 6-pyr*H*, $J_{5,6}$ = 6.5, J_{PtH} = 12.8 Hz, 1 H); IR (KBr) 1740 vs (C=O), 1127 m (C—O), 762, 727 cm^{-1}. Anal. Calcd for $\mathrm{C_{20}H_{22}N_2Cl_2O_8Pt}$: C, 35.10; H, 3.24; N, 4.09. Found: C, 34.90; H, 3.50; N, 4.06.

***af*-Dichloro-*de*-bis(dimethyl malonato-*C*)-*bc*-(1,10-phenanthroline)platinum(IV) (20)** was prepared by both methods from 16: method A, 59%; method B, 69%; mp >300 °C; ^{1}H NMR δ 3.73 (ss,[57] C*H*$_3$, J_{PtH} = 2.7 Hz, 6 H), 5.09 (ss,[57] C*H*, J_{PtH} = 88.7 Hz, 1 H), 7.95 (s, 5-phen*H*, 1 H), 8.01 (dd, 3-phen*H*, $J_{3,4}$ = 8.2, $J_{2,3}$ = 5.5 Hz, 1 H), 8.50 (dd, 4-phen*H*, $J_{3,4}$ = 8.2, $J_{2,4}$

= 1.3 Hz, 1 H), 10.88 (ds,[57] 2-phen*H*, $J_{2,3}$ = 5.5, J_{PtH} = 14.6 Hz, 1 H); IR (KBr) 1744 (C=O), 1129 (C—O), 847, 718 cm^{-1}. Anal. Calcd for $C_{22}H_{22}N_2Cl_2O_8Pt$: C, 37.30; H, 3.13; N, 3.95. Found: C, 37.42; H, 3.22, N, 3.76.

When method B was used with 16, the cis complex **21** was also isolated. ***cis*-Dichloro-*cis*(dimethyl malonato-*C*)(1,10-phenanthroline)platinum(IV) (21)**: 5%; mp >260 °C; ^{1}H NMR δ 2.56 (ss,[57] CH_3, J_{PtH} = 2.2 Hz, 3 H), 3.58 (ss,[57] CH_3, J_{PtH} = 2.5 Hz, 3 H), 3.73 (s, CH_3, J_{PtH} = 2.2 Hz, 3 H), 3.84 (s, CH_3, J_{PtH} = 2.2 Hz, 3 H), 4.52 (ss,[57] C*H*, J_{PtH} = 85.6 Hz, 1 H), 5.88 (ss,[57] C*H*, J_{PtH} = 98.9 Hz, 1 H), 7.92–8.16 (m, 3,5,6,8-phen*H*, 4 H), 8.59 (dd, 7-phen*H*, $J_{7,8}$ = 8.2, $J_{7,9}$ = 1.2 Hz, 1 H), 8.63 (dd, 4-phen*H*, $J_{3,4}$ = 8.3, $J_{2,4}$ = 1.3 Hz, 1 H), 9.60 (dds,[57] 2-phen*H*, $J_{2,3}$ = 5.4, $J_{2,4}$ = 1.3, J_{PtH} = 14.9 Hz, 1 H), 10.86 (dds,[57] 9-phen*H*, $J_{8,9}$ = 5.7, $J_{7,9}$ = 1.2, J_{PtH} = 30.4 Hz, 1 H) (insufficient sample for CHN analysis).

Attempt To Synthesize Pt(phen)(dmm)$_4$ (22). Dimethyl malonate (80 mg, 610 μmol) and anhydrous K_2CO_3 (134 mg, 970 μmol) were added to a solution of freshly prepared Pt(phen)(dmm)$_2$Br$_2$ (18) (75 mg, 90 μmol) in DMF (10 mL), and the solution was heated to 90 °C for 12 h. The DMF and excess malonate were then removed in vacuo, and the remaining solid was extracted with $CHCl_3$. After filtration and removal of the $CHCl_3$ the product was purified by flash-dry chromatography[56] eluting first with $CHCl_3$ and then with 30% MeOAc/$CHCl_3$. The $CHCl_3$ fraction afforded (88%) **dimethyl 2,3-bis(methoxycarbonyl)butanedioate**,[58] as determined by ^{1}H NMR: 22 mg.

The MeOAc/$CHCl_3$ fraction afforded (77%) **bis(dimethyl malonato-*C*)(1,10-phenanthroline)platinum(II) (16)**: 47 mg.

Reaction of Pt(phen)(ddm)$_2$Br$_2$ (18) with NaOH. Pt(phen)(dmm)$_2$Br$_2$ (18) (40 mg, 50 μmol) in CH_2Cl_2 (5 mL) was added to a solution of NaOH (52 mg, 1.3 mmol) in EtOH (5 mL). The mixture was stirred for 15 min at 25 °C. More CH_2Cl_2 was added and the solution washed twice with aqueous saturated NaCl. The CH_2Cl_2 solution was then dried over anhydrous $MgSO_4$ and the solvent removed to give Pt(phen)(dmm)$_2$ (**16**) as a yellow solid (8 mg, 25%).

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Supplementary Material Available: Listings of bond distances, bond angles, coordinates for H atoms, and anisotropic thermal parameters for **10a**, **10b**, and **11** (16 pages); listings of structure factor amplitudes for **10a**, **10b**, and **11** (70 pages). Ordering information is given on any current masthead page.

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Cooperative Effects in π-Ligand Bridged Binuclear Complexes. 8. Cyclic Voltammetric, NMR, and ESR Spectroscopic Studies of Electron-Poor Synfacial Bis((η^5-cyclopentadienyl)metal) μ-Cyclooctatetraene Complexes of Chromium and Vanadium

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Electron-poor (∑ve < 34) (ve = valence electron) synfacial μ-Cot (Cot = cyclooctatetraene) complexes of the general composition X(Cp′$_2$MM′)(μ-Cot) (Cp′ = C_5H_4; X = H,H, CH_2, SiMe$_2$, GeMe$_2$; M = M′ = V, **1a–d**; M = M′ = Cr, **2a–d**; M = V, M′ = Cr, X = H,H, **3**) are studied by cyclic voltammetry and ESR as well as NMR spectroscopy. Except for (CpV)$_2$(μ-Cot) (**1a**) (Cp = C_5H_5) two electrochemically reversible redox pairs are found involving diffusion-controlled one-electron transfers: all compounds show a reduction step at −2 V (vs SCE) and in **2a–d** as well as in **3** an oxidation step occurs at about −0.7 V (vs SCE) whereas for **1b–d** the oxidation is not observed before $E°$ > 0 V (vs SCE). A second electrochemically reversible redox pair, 1+/2+, is measured at $E°$ > 0.3 V (vs SCE) for the dichromium complexes **2a–d**. All species within 28 ≤ ∑ve ≤ 31 are stable enough to be studied by NMR and ESR spectroscopy. The homobinuclear radical species with 29 and 31 ve contain an unpaired electron completely delocalized over both metal centers. In contrast to it, the unpaired electron in the mixed complex is localized on the V center mainly. From NMR spectroscopic results the 30 ve complexes are purely diamagnetic whereas the 28 ve compounds possess a low-lying triplet state (Δ*H* = 22–24 kJ mol^{-1}). This low-lying triplet state is explained by a qualitative MO diagram indicating only a small splitting between the HOMO (δMO) and LUMO (δ*MO). The ^{1}H NMR spectroscopic data confirm a strong diamagnetic anisotropy of the metal–metal multiple bond in **1a–d** (Δχ > 2000 × 10^{-36} m^3 molecule^{-1}) and **2a–d** (Δχ > 3000 × 10^{-36} m^3 molecule^{-1}).

Introduction

We reported the synthesis and structures as well as some magnetic properties of the homobinuclear μ-Cot complexes of the type (CpM)$_2$(μ-Cot) (M = V, **1a**; M = Cr, **2a**) in two recent papers.[2,3]

Two facts mainly prevail on us about getting more information on the metal–metal interaction in complexes of type **1a** and **2a**: (i) **1a** and **2a** have nearly the same structure and the intermetal distance in **1a** is about 5 pm longer than in **2a**, although the bond order in **1a** might be a triple bond, whereas the bond order in **2a** is a double bond with respect to the EAN rule and their magnetic

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