Organoplatinum(IV) Polymers and Model Complexes by Oxidative Addition of Bromoacetate Esters

Sudhir Achar,[1a] John D. Scott,[1b] Jagadese J. Vittal,[1a] and
Richard J. Puddephatt*,[1a]

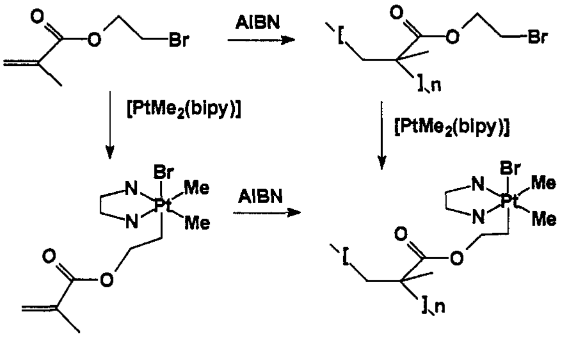
*Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7,
and Research and Development Laboratories, 3M Canada Inc.,
CP Box 5757, London, Ontario, Canada N6A 4T1*

Received June 21, 1993®

The oxidative addition of bromoacetic acid or its derivatives to [$PtMe_2$(bpy)], **1a**, bpy = 2,2′-bipyridine, or the new complex [$PtMe_2(bu_2bpy)$], **1b**, bu_2bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine, gives the complexes [$PtBrMe_2(CH_2X)$(NN)] [(NN = bpy) X = CO_2Me (**2**), X = CO_2Et (**3**), X = CO_2H (**4**), X = C≡N (**5**), X = $CONH_2$ (**6**); (NN = bu_2bpy) X = $CO_2CH{=}CH_2$ (**7**)]. Similarly, the diester $BrCH_2CO_2CH_2CH_2O_2CCH_2Br$ reacted with [$PtMe_2$(NN)] to give the bridged dimer [{$PtBrMe_2$(NN)}$_2$(μ-$CH_2CO_2CH_2CH_2O_2CCH_2$)] [**8**, NN = bpy; **9**, NN = bu_2bpy]. Many of the complexes **2**–**9** were shown by NMR to exist as a mixture of two isomers, the major or sole product corresponding to that of *trans* oxidative addition. Complexes **2** and **9** were also characterized by X-ray structure determinations, which showed that the preferred conformation has the ester group lying above the flat diimine ligand. This leads to a helical conformation for complex **9**. Free radical polymerization of complex **7** gave the polymer [{$PtBrMe_2(NN)(CH_2CO_2)$}$CHCH_2$]$_n$, **10a**, NN = bu_2bpy, in which the organoplatinum groups are present as substituents on the acetate groups of the poly(vinyl acetate) chain. A similar polymer, **10b**, was prepared by esterification of poly(vinyl alcohol) to poly(vinyl bromoacetate) followed by its oxidative addition to an excess of [$PtMe_2(bu_2bpy)$]. The bu_2bpy ligand is shown to be useful in giving enhanced solubility to the platinum complexes.

In most polymers containing pendant transition metal complexes, the metal is bound to the polymer by coordination to amine, phosphine, η-cyclopentadienyl, η-arene, or related donors.[2] The polymers may be prepared either by incorporation of a polymerizable functionality into the metal complex monomer followed by polymerization or by functionalizing an organic polymer with the required donor groups and then using these to substitute for a ligand on a monomeric transition metal complex.[2] This synthetic methodology can be extended by using oxidative addition to prepare functionalized transition metal monomers or polymers. These reactions differ from those discussed above since functionalization occurs with an increase in oxidation state of the transition metal by two units.[3] In addition, the metal will be bonded to the polymer by a σ-bond rather than by a donor–acceptor bond. Some examples of this synthetic method, which take advantage of the high reactivity of [$PtMe_2$(bpy)] toward oxidative addition of alkyl halides, have been reported and a simplified one is shown in Scheme I.[4] Free radical polymerization of the monomer 2-bromoethyl methacrylate gives the organic polymer which oxidatively adds to [$PtMe_2$(bpy)] to give the platinated polymer or, alternatively, oxidative addition of the monomer to [$PtMe_2$(bpy)] gives the platinated monomer which undergoes free radical polymerization to the platinated polymer. This paper gives a full report of an example of this method of preparing organometallic polymers in which the organic monomer is a vinyl ester of bromoacetic acid rather than the bromoalkyl ester of methacrylic acid shown in Scheme I. Also described are a mononuclear and a binuclear model complex containing the functional groups present in the polymeric platinum(IV) complexes.

Scheme I[a]



[a] AIBN = azobis(isobutyronitrile).

Results and Discussion

Mononuclear Complexes. The complex [$PtMe_2$(bpy)], bpy = 2,2′-bipyridine, **1a**, is very reactive in oxidative addition, but the products often have limited

---

® Abstract published in *Advance ACS Abstracts*, October 15, 1993.

[1] (a) University of Western Ontario. (b) 3M Canada.

[2] (a) Kaneko, M.; Tsuchida, E. *J. Polym. Sci., Macromol. Rev.* 1981, *16*, 397. (b) Pittman, C. U.; Carraher, C. E., Jr.; Reynolds, J. R. *Encyclopedia of Polymer Science and Engineering*, 11th ed.; Wiley: New York, 1988; Vol. 10, p 451. (c) Carraher, C. E. Jr.; Manek, T. A.; Giron, D. J.; Trombley, M. L.; Casberg, K. M.; Scott, W. J. In *New Monomers and Polymers*; Culbertson, W. M., Pittman, C. U., Jr., Eds.; Plenum: New York, 1984; p 133. (d) Ahmed, A. K.; Jawad, J. K.; Rashied, M. A. M. *Eur. Polym. J.* 1987, *23*, 163. (e) Pittman, C. U., Jr. *Organomet. React. Synth.* 1977, *6*, 1. (f) Sekiya, A.; Stille, J. K. *J. Am. Chem. Soc.* 1981, *103*, 5096.

[3] Stille, J. K. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1985; Vol. II, p 625.

[4] Achar, S.; Scott, J. D.; Puddephatt, R. J. *Organometallics* 1992, *11*, 2325.

0276-7333/93/2312-4592$04.00/0

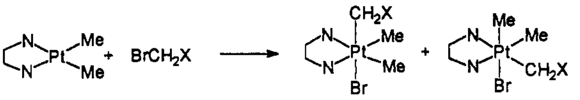
Table I. Selected NMR Data and Isomer Ratios for Complexes 2–9[a]

	trans		*cis*		
complex	δ(MePt), *J*(PtH)	δ(CH_2Pt), *J*(PtH)	δ(MePtBr), *J*(PtH)	δ(MePtN), *J*(PtH)	ratio *trans*:*cis*
2[b]	1.43, 69	2.01, 96	0.58, 69	1.54, 69	9:1
3[b]	1.44, 69	2.00, 96	0.56, 70	1.55, 70	9:1
4[b]	1.45, 69	1.99, 97	0.69, 70	1.53, 70	7:1
5[c]	1.48, 69	1.69, 93			*f*
6[d]	1.31, 69	1.88, 93	0.64, 75	1.41, 75	4:1
7[c]	1.47, 68	2.12, 98	0.77, 72	*g*	7:1
8[e]	1.40, 69	2.00, 98	0.44, 69	1.44, 69	9:1
9[c]	1.46, 68	2.07, 99	0.51, 72	1.42, 68	9:1

[a] *J* in Hz. [b] Solvent acetone-d^6. [c] Solvent CD_2Cl_2. [d] Solvent dmso-d_6. [e] Solvent CD_3CN. [f] *cis* isomer absent. [g] Peak obscured.

solubility.[5] To overcome this solubility problem, the new complex [$PtMe_2(bu_2bpy)$], bu_2bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine, **1b**, was prepared. Both **1a** and **1b** are red solids, the color arising from the presence of a metal-to-ligand charge transfer (MLCT) band in the visible region of the spectrum.[5] Generally, oxidative addition of alkyl halides, RX, to red **1** gives pale yellow [$PtXRMe_2$(bpy)] or [$PtXRMe_2(bu_2bpy)$], since the MLCT band moves to higher energy in the platinum(IV) products. In addition, the methylplatinum coupling constant, observed in the ^1H NMR spectrum, decreases from 84–86 Hz in **1** to 69–72 Hz in the platinum(IV) products. Both features are useful in monitoring the oxidative addition reactions and in characterizing the products.[5]

As a model reaction, the oxidative addition of methyl bromoacetate to [$PtMe_2$(bpy)] was studied. The products of *trans* and *cis* oxidative addition, **2a** and **2b**, respectively, were formed in a 9:1 ratio (eq 1, Table I). The *trans* isomer


(1)

NN = bipy, X = CO_2Me	**2a**	**2b**
NN = bipy, X = CO_2Et	**3a**	**3b**
NN = bipy, X = CO_2H	**4a**	**4b**
NN = bipy, X = CN	**5a**	**5b**
NN = bipy, X = $CONH_2$	**6a**	**6b**
NN = bu_2bipy, X = $CO_2CH{=}CH_2$	**7a**	**7b**

2a has δ(MePt) = 1.43, ^2J(PtH) = 69 Hz, while **2b** has δ(MePt, *trans* to Br) = 0.58 and δ(MePt, *trans* to N) = 1.54, each with ^2J(PtH) = 69 Hz. The presence of the Pt–CH_2 group in **2a** was indicated by a singlet at δ = 2.01, with ^2J(PtH) = 96 Hz, but this resonance was not resolved for **2b**.

Complex **2a** was also characterized by an X-ray structure determination. The molecular structure is shown in Figure 1, and selected bond distances and angles are given in Table II. The molecular dimensions do not require discussion, but it is significant that the conformation of the $PtCH_2CO_2Me$ group is such that the ester group lies beneath the flat bipyridine ring, presumably in order to minimize steric hindrance. The methoxy group, in the most stable conformation, therefore lies in the diamagnetic ring shielding region of the bpy ligand and appears in the ^1H NMR at δ = 2.67. A similar conformation of an acetyl group has been observed in [$PtMe_3\{CH(COMe)_2\}$(bpy)].[6a] There are no very short intramolecular contacts in **2a**, and so a low barrier to rotation about the Pt–CH_2 bond is expected.

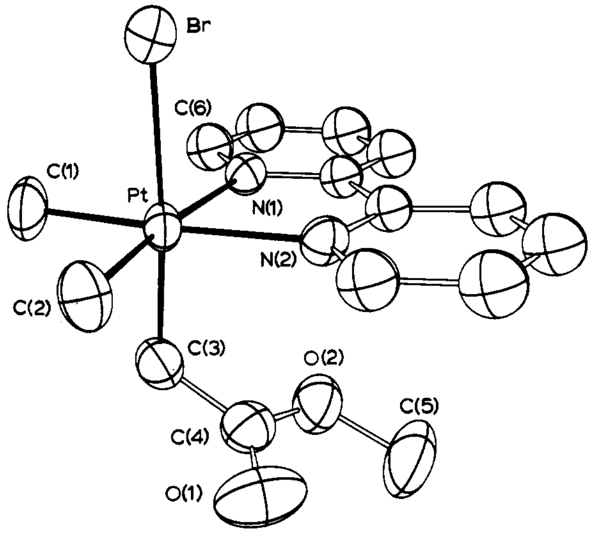


Figure 1. ORTEP view of compound **2a** showing 50% thermal ellipsoids. The hydrogen atoms are omitted for clarity.

Table II. Bond Distances (Å) and Angles (deg) for 2a

Br–Pt	2.5663(6)	C(1)–Pt	2.055(5)
C(2)–Pt	2.054(5)	C(3)–Pt	2.076(5)
N(1)–Pt	2.165(4)	N(2)–Pt	2.159(4)
C(4)–C(3)	1.483(7)	O(1)–C(4)	1.207(6)
O(2)–C(4)	1.343(6)	C(5)–O(2)	1.455(7)
C(6)–N(1)	1.345(6)	C(10)–N(1)	1.356(6)
C(11)–N(2)	1.350(5)	C(15)–N(2)	1.345(6)
C(7)–C(6)	1.376(7)	C(8)–C(7)	1.374(8)
C(9)–C(8)	1.365(7)	C(10)–C(9)	1.388(6)
C(11)–C(10)	1.467(6)	C(12)–C(11)	1.396(7)
C(13)–C(12)	1.374(7)	C(14)–C(13)	1.350(7)
C(15)–C(14)	1.410(8)		

C(1)–Pt–Br	90.26(16)	C(2)–Pt–Br	91.04(15)
C(2)–Pt–C(1)	89.05(23)	C(3)–Pt–Br	175.45(14)
C(3)–Pt–C(1)	85.20(21)	C(3)–Pt–C(2)	88.52(21)
N(1)–Pt–Br	90.62(10)	N(1)–Pt–C(1)	97.84(20)
N(1)–Pt–C(2)	172.91(18)	N(1)–Pt–C(3)	90.36(17)
N(2)–Pt–Br	89.25(10)	N(2)–Pt–C(1)	174.63(19)
N(2)–Pt–C(2)	96.31(18)	N(2)–Pt–C(3)	95.30(17)
N(2)–Pt–N(1)	76.82(14)	C(4)–C(3)–Pt	111.3(3)
O(1)–C(4)–C(3)	126.0(6)	O(2)–C(4)–C(3)	111.9(5)
O(2)–C(4)–O(1)	122.1(6)	C(5)–O(2)–C(4)	113.4(5)
C(6)–N(1)–Pt	126.1(3)	C(10)–N(1)–Pt	114.8(3)
C(10)–N(1)–C(6)	119.0(4)	C(11)–N(2)–Pt	114.7(3)
C(15)–N(2)–Pt	125.3(3)	C(15)–N(2)–C(11)	120.0(4)
C(7)–C(6)–N(1)	122.2(5)	C(8)–C(7)–C(6)	118.2(6)
C(9)–C(8)–C(7)	120.7(5)	C(10)–C(9)–C(8)	118.9(5)
C(9)–C(10)–N(1)	120.9(4)	C(11)–C(10)–N(1)	116.3(4)
C(11)–C(10)–C(9)	122.8(4)	C(10)–C(11)–N(2)	117.3(4)
C(12)–C(11)–N(2)	120.7(4)	C(12)–C(11)–C(10)	122.0(4)
C(13)–C(12)–C(11)	119.1(5)	C(14)–C(13)–C(12)	120.5(5)
C(15)–C(14)–C(13)	119.1(6)	C(14)–C(15)–N(2)	120.6(5)

The oxidative addition of bromoacetic acid derivatives is a general reaction, as illustrated by the examples in eq 1 and Table I. The formation of **4** by oxidative addition of bromoacetic acid is particularly noteworthy. The complex [$PtMe_2$(bpy)] reacts with many carboxylic acids RCO_2H to give methane and [$PtMe(O_2CR)$(bpy)], and most other alkylplatinum(II) complexes react in an

---

(5) (a) Monaghan, P. K.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1988**, 595. (b) Crespo, M.; Puddephatt, R. J. *Organometallics* **1987**, *6*, 2548. (c) Monaghan, P. K.; Puddephatt, R. J. *Organometallics* **1985**, *4*, 1405. (d) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 1538. (e) Scott, J. D.; Crespo, M.; Anderson, C. M.; Puddephatt, R. J. *Organometallics* **1987**, *6*, 1772.

(6) (a) Swallow, A. G.; Truter, M. R. *Proc. R. Soc. London, Ser. A* **1962**, *266*, 527. (b) Aye, K.-T.; Puddephatt, R. J. Unpublished work.

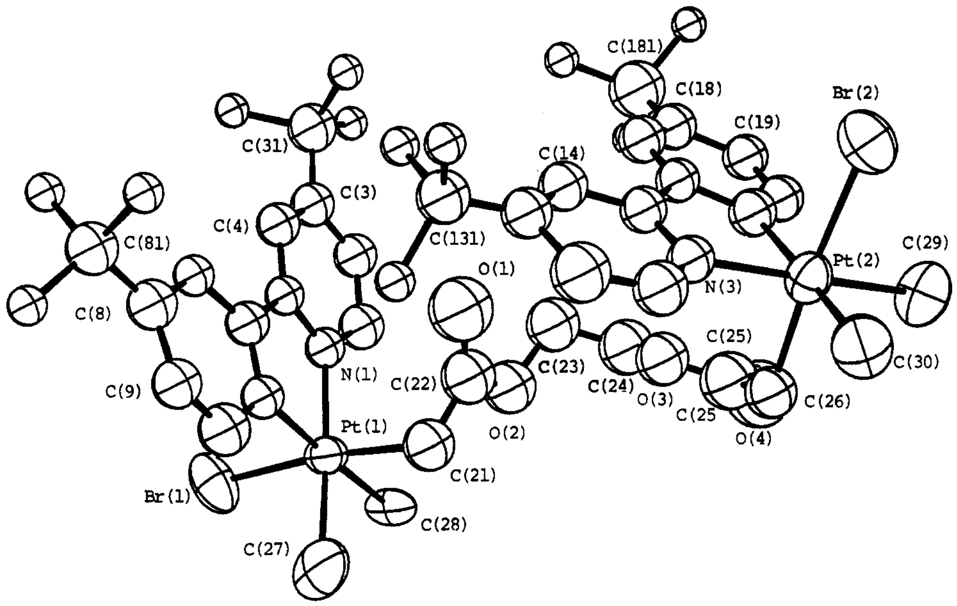


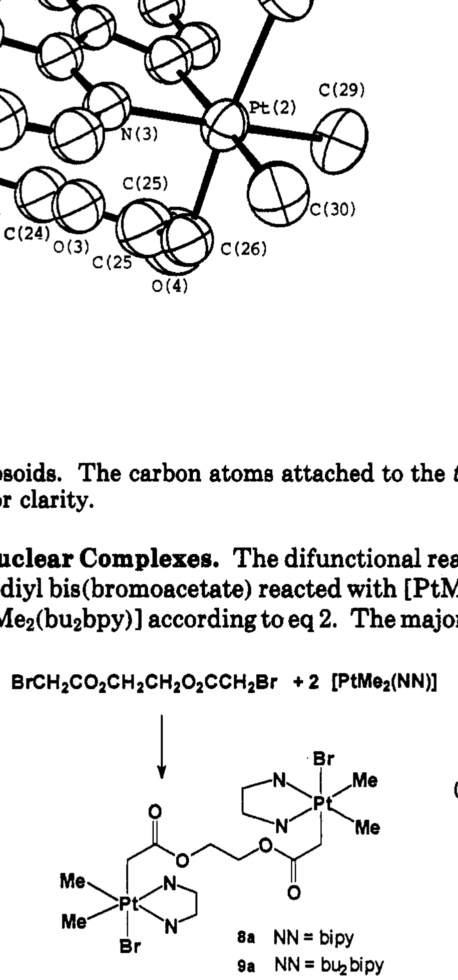
Figure 2. ORTEP view of compound **9a** showing 50% probability ellipsoids. The carbon atoms attached to the *tert*-butyl groups are given a small radius, and the hydrogen atoms are omitted for clarity.

analogous way.[6b] None of this reaction could be detected with bromoacetic acid, indicating that the oxidative addition (eq 1) must be much faster than the usual methyl–platinum acid cleavage reaction. Since methyl–platinum(IV) bonds are stable to carboxylic acids, the product **4** is a stable complex and is a rare example of an organometallic complex with a carboxylic acid substituent; most known examples of alkylmetal complexes with carboxylic acid functionality are with the main group elements silicon and germanium.[7] The IR spectrum contained bands due to ν(OH) at 2640 and 2550 (br) cm^{-1} and ν(CO) at 1662 cm^{-1}, suggesting that the organometallic carboxylic acid exists as a hydrogen-bonded dimer typical of organic carboxylic acids.[8]

The oxidative addition of bromoacetamide to give **6** is similarly noteworthy since there are few organometallic complexes with acid amide functionality.[9] Complex **6** was very sparingly soluble in common organic solvents, but good NMR data were obtained in dmso-d_6 solution. Each isomer **6a** and **6b** gave two well-defined singlets due to the nonequivalent amide NH_2 protons (experimental), indicating that rotation about the C–N bond is slow and hence that partial C–N double bonding, which is present in acid amides and which leads to a barrier to rotation about the C–N bond, is not affected by the platinum substituent. In support, the bands in the IR spectrum due to the amide group [ν(NH) = 3393 and 3177 cm^{-1}, ν(CO) = 1643 cm^{-1}] are similar to those in the parent bromoacetamide [ν(NH) = 3395 and 3175 cm^{-1}, ν(CO) = 1655 cm^{-1}]. These frequencies are in the region expected for hydrogen-bonded dimers of the acetamide derivative.[9]

As expected from the above model reactions, vinyl bromoacetate reacted easily with [$PtMe_2(bu_2bpy)$] to give the oxidative addition product **7**. The product is formed in high yield and the *tert*-butyl substituents ensure high solubility; hence **7** should be a useful polymerizable monomer.

Binuclear Complexes. The difunctional reagent 1,2-ethanediyl bis(bromoacetate) reacted with [$PtMe_2(bpy)$] or [$PtMe_2(bu_2bpy)$] according to eq 2. The major product



(2)

was the *trans,trans* product shown, but minor resonances in the ^{1}H NMR spectra could be attributed to the *trans,cis* isomer (Table I). For the *trans,cis* isomer, three MePt resonances are expected in a 2:1:1 ratio. Only two were observed in a 1:1 ratio, so it is assumed that the resonance due to the MePt groups at the *trans* site is obscured by the much more intense resonance from the *trans,trans* isomer. It is possible that the minor isomer is the *cis,cis* isomer, but this is considered improbable.

Characterization of the *trans,trans* isomer **9** has been confirmed by an X-ray structure determination. Selected bond distances and angles are given in Table III. This structure is relevant as a model for a polymeric derivative and so the conformation is of interest. At both platinum centers the planar carboxyl group is oriented beneath the planar bu_2bpy group. However, the orientation with the C═O group below the ring is different from that in the mononuclear complex **2a**, in which the C—O—Me group was more central. The angle between planes defined by the carboxyl group and the bpy group is 25° but averages 30° in **9**, probably due to greater steric effects. In complex **9** the angles between the two carboxyl planes and two bpy planes are 93 and 140°, respectively. It seems that the orienting effect of the planar bpy and carboxyl groups leads to a helical structure for the bridging group. The

---

[7] Steward, O. W.; Heider, G. L.; Johnson, J. S. *J. Organomet. Chem.* **1979**, *168*, 33.

[8] Maréchal, Y. *J. Chem. Phys.* **1987**, *87*, 6344.

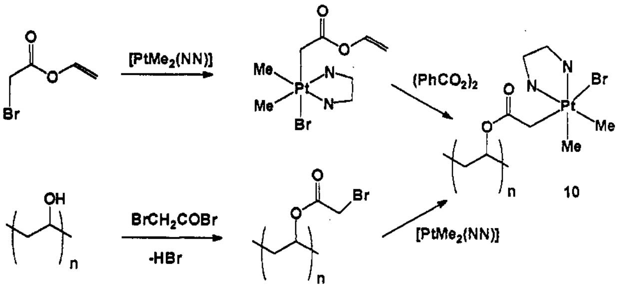
[9] (a) Troitino, D.; De La Blanca, E. S.; Garcia, M. V. *Spectrochim. Acta* **1990**, *46A*, 1281. (b) Kerridge, D. H. *Chem. Soc. Rev.* **1988**, *17*, 181.

Table III. Bond Distances (Å) and Angles (deg) for 9a

Pt(1)–Br(1)	2.5137(2)	Pt(2)–Br(2)	2.5431(2)
Pt(1)–N(1)	2.063(1)	Pt(1)–N(2)	2.078(1)
Pt(2)–N(3)	2.082(1)	Pt(2)–N(4)	2.050(1)
Pt(1)–C(21)	2.038(1)	Pt(2)–C(26)	2.148(1)
Pt(1)–C(27)	2.164(2)	Pt(1)–C(28)	2.104(1)
Pt(2)–C(29)	2.174(1)	Pt(2)–C(30)	2.072(1)
N(1)–C(1)	1.432(2)	C(1)–C(2)	1.405(2)
C(2)–C(3)	1.384(2)	C(3)–C(4)	1.384(2)
C(3)–C(31)	1.519(2)	C(4)–C(5)	1.364(2)
N(1)–C(5)	1.354(1)	C(5)–C(6)	1.455(2)
N(2)–C(6)	1.330(1)	C(6)–C(7)	1.407(1)
C(7)–C(8)	1.448(2)	C(8)–C(9)	1.396(2)
C(8)–C(81)	1.496(2)	C(9)–C(10)	1.393(2)
N(2)–C(10)	1.340(2)	N(3)–C(11)	1.338(2)
C(11)–C(12)	1.347(2)	C(12)–C(13)	1.488(2)
C(13)–C(14)	1.394(2)	C(13)–C(131)	1.399(2)
C(14)–C(15)	1.429(2)	N(3)–C(15)	1.343(1)
C(14)–C(15)	1.429(2)	C(15)–C(16)	1.447(2)
N(4)–C(16)	1.421(1)	C(16)–C(17)	1.375(2)
C(17)–C(18)	1.403(2)	C(18)–C(19)	1.407(2)
C(18)–C(181)	1.463(2)	C(19)–C(20)	1.339(2)
N(4)–C(20)	1.319(1)	C(21)–C(22)	1.420(2)
C(23)–C(24)	1.408(2)	C(25)–C(26)	1.465(2)
O(1)–C(22)	1.260(2)	O(2)–C(22)	1.337(2)
O(2)–C(23)	1.468(2)	O(3)–C(24)	1.415(2)
O(3)–C(25)	1.220(2)	O(4)–C(25)	1.311(2)

N(1)–Pt(1)–Br(1)	89.59(3)	N(2)–Pt(1)–Br(1)	92.72(3)
N(2)–Pt(1)–N(1)	77.87(4)	C(21)–Pt(1)–Br(1)	172.05(5)
C(21)–Pt(1)–N(1)	95.75(5)	C(21)–Pt(1)–N(2)	94.15(5)
C(27)–Pt(1)–Br(1)	89.95(6)	C(27)–Pt(1)–N(1)	175.12(5)
C(27)–Pt(1)–N(2)	97.30(6)	C(27)–Pt(1)–C(21)	85.22(7)
C(28)–Pt(1)–Br(1)	89.91(4)	C(28)–Pt(1)–N(1)	101.23(4)
C(28)–Pt(1)–N(2)	177.21(5)	C(28)–Pt(1)–C(21)	83.29(6)
C(28)–Pt(1)–C(27)	83.63(6)	N(3)–Pt(2)–Br(2)	90.83(3)
N(4)–Pt(2)–Br(2)	89.94(3)	N(4)–Pt(2)–N(3)	78.25(4)
C(26)–Pt(2)–Br(2)	173.57(4)	C(26)–Pt(2)–N(3)	91.56(5)
C(26)–Pt(2)–N(4)	96.39(5)	C(29)–Pt(2)–Br(2)	90.88(4)
C(29)–Pt(2)–N(3)	174.84(5)	C(29)–Pt(2)–N(4)	96.88(5)
C(29)–Pt(2)–C(26)	87.26(6)	C(30)–Pt(2)–Br(2)	88.97(5)
C(30)–Pt(2)–N(3)	97.27(6)	C(30)–Pt(2)–N(4)	175.38(6)
C(30)–Pt(2)–C(26)	84.81(6)	C(30)–Pt(2)–C(29)	87.63(6)
C(1)–N(1)–Pt(1)	124.8(1)	C(5)–N(1)–Pt(1)	116.4(1)
C(6)–N(2)–Pt(1)	114.8(1)	C(10)–N(2)–Pt(1)	126.2(1)
C(11)–N(3)–Pt(2)	126.2(1)	C(15)–N(3)–Pt(2)	115.6(1)
C(16)–N(4)–Pt(2)	115.5(1)	C(20)–N(4)–Pt(2)	127.1(1)
C(5)–N(1)–C(1)	118.8(1)	C(10)–N(2)–C(6)	118.3(1)
C(15)–N(3)–C(11)	117.9(1)	C(20)–N(4)–C(16)	117.4(1)
C(2)–C(1)–N(1)	118.5(1)	C(3)–C(2)–C(1)	121.4(1)
C(4)–C(3)–C(2)	117.2(1)	C(31)–C(3)–C(2)	119.5(1)
C(31)–C(3)–C(4)	122.7(1)	C(5)–C(4)–C(3)	122.7(1)
C(4)–C(5)–N(1)	121.2(1)	C(6)–C(5)–N(1)	113.6(1)
C(6)–C(5)–C(4)	125.3(1)	C(5)–C(6)–N(2)	117.0(1)
C(7)–C(6)–N(2)	121.8(1)	C(7)–C(6)–C(5)	121.2(1)
C(8)–C(7)–C(6)	121.1(1)	C(9)–C(8)–C(7)	113.5(1)
C(81)–C(8)–C(7)	120.5(1)	C(81)–C(8)–C(9)	125.7(1)
C(10)–C(9)–C(8)	121.0(1)	C(9)–C(10)–N(2)	122.8(1)
C(12)–C(11)–N(3)	124.0(1)	C(13)–C(12)–C(11)	120.6(1)
C(14)–C(13)–C(12)	113.9(1)	C(131)–C(13)–C(12)	119.6(1)
C(131)–C(13)–C(14)	126.2(1)	C(15)–C(14)–C(13)	120.3(1)
C(14)–C(15)–N(3)	122.9(1)	C(16)–C(15)–N(3)	116.8(1)
C(16)–C(15)–C(14)	120.3(1)	C(15)–C(16)–N(4)	112.8(1)
C(17)–C(16)–N(4)	118.0(1)	C(17)–C(16)–C(15)	128.2(1)
C(18)–C(17)–C(16)	124.7(1)	C(19)–C(18)–C(17)	112.9(1)
C(181)–C(18)–C(17)	125.1(1)	C(181)–C(18)–C(19)	122.0(1)
C(20)–C(29)–C(18)	122.3(1)	C(19)–C(20)–N(4)	124.6(1)
C(23)–O(2)–C(22)	118.1(1)	C(25)–O(3)–C(24)	120.3(1)
C(22)–C(21)–Pt(1)	112.4(1)	O(2)–C(22)–O(1)	120.0(2)
C(21)–C(22)–O(1)	126.9(2)	C(21)–C(22)–O(2)	112.8(1)
C(24)–C(23)–O(2)	109.1(1)	C(23)–C(24)–O(3)	108.8(1)
O(4)–C(25)–O(3)	116.3(2)	C(26)–C(25)–O(3)	119.1(2)
C(26)–C(25)–O(4)	124.6(2)	C(25)–C(26)–Pt(2)	111.0(1)
C(32)–C(31)–C(3)	112.7(1)	C(33)–C(31)–C(3)	110.3(1)
C(34)–C(31)–C(3)	104.7(1)	C(82)–C(81)–C(8)	107.9(1)
C(83)–C(81)–C(8)	112.3(1)	C(84)–C(81)–C(8)	107.6(1)
C(132)–C(131)–C(13)	109.8(1)	C(133)–C(131)–C(13)	107.6(1)
C(134)–C(131)–C(13)	110.5(1)	C(182)–C(181)–C(18)	112.2(1)
C(183)–C(181)–C(18)	111.6(1)	C(184)–C(181)–C(18)	103.9(1)

Scheme II[a]



[a] NN = bu$_2$bpy.

eight-atom bridge between metal atoms is unusual in alkanediyl bridged complexes.[10]

Polymeric Complexes. The free radical polymerization of the monomer **7** was carried out by using the initiator dibenzoyl peroxide in *tert*-butyl alcohol at 75 °C to give the polymer **10a** (Scheme II). The use of *tert*-butyl alcohol for polymerization of vinyl monomers such as vinyl acetate is well-known and is advantageous because its chain-transfer activity is very low.[11] The ^{1}H NMR spectrum of polymer **10a** contained only one very broad peak due to all the aliphatic protons at $\delta = 1.5$, but three broad resonances due to bpy protons were observed at $\delta = 7.6$, 8.2, and 8.7. The integral was fully consistent with the proposed structure. Unfortunately, the solubility was too low for solution molecular weight measurement.

Because such limited characterization of polymer **10a** was possible, other routes to the polymer were explored. Poly(vinyl bromoacetate) could obviously be used as a precursor to **10** (Scheme II). Attempts to prepare this organic polymer by polymerization of vinyl bromoacetate were unsuccessful, but it could be prepared by reaction of poly(vinyl alcohol) (average $M = 50\,000$) with bromoacetyl bromide.[12] Both elemental and NMR analysis of the polymer **11** indicated that essentially all of the hydroxyl groups in the poly(vinyl alcohol) were functionalized. Subsequent oxidative addition to excess [PtMe$_2$(bu$_2$bpy)] then gave the polymer **10b**. The elemental analysis indicated that essentially all of the C–Br bonds oxidatively added. The ^{1}H NMR spectra of **10a** and **10b** were essentially identical in number of peaks, peak widths, chemical shifts, and areas. The inability to resolve the ^{1}H NMR peaks due to MePt, *t*-Bu, and other aliphatic groups was disappointing, since a direct proof of the presence of the methylplatinum groups by ^{1}H NMR was thus precluded. To prove the presence of methylplatinum groups in **10**, the oxidative addition of poly(vinyl bromoacetate) to [Pt(CD$_3$)$_2$(bu$_2$bpy)] was carried out. The polymer **10-*d*$_6$** was characterized by two broad resonances in the ^{2}H NMR. On the basis of the NMR data of the model complexes (Table I), the more intense resonance at $\delta = 1.4$ is assigned to the CD$_3$Pt groups *trans* to nitrogen while a less intense resonance at $\delta = 0.6$ is assigned to CD$_3$ groups *trans* to bromide. These data clearly confirm the presence of CD$_3$Pt groups in the polymer and also show that some of the platinum(IV) centers arise from *cis* oxidative addition, as expected from the model complexes **2**, **8**, and **9**.

---

[10] (a) Holton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. I. *Chem. Rev.* **1983**, *83*, 135. (b) Moss, J. R.; Scott, L. G. *Coord. Chem. Rev.* **1984**, *60*, 171.

[11] Sandler, S. R.; Karo, W. *Organic Chemistry. A Series of Monographs*; Academic Press: New York, 1980; Vol. 29, p 206.

[12] Carpov, P. A.; Dragan, D. *Angew. Makromol. Chem.* **1972**, *24*, 101.

Table IV. Thermal Properties of Complexes and Polymers

compd	MP onset from DSC/°C	decomp range/ °C (wt loss/%) from TGA[a]	residue/%[b] found (temp/ °C), % calc
1b	259	164–290 (52)	39.5 (660), 39.5
2	217	227–570 (43)	48 (695), 36.5
7	175	205–446 (61)	37 (570), 29.6
8	184	235–654 (45)	40 (795), 36.5
9	226	254–434 (59)	35 (600), 30.2
11	237	223–365 (83)	11 (500), 0
10a	*c*	220–423 (60)	32 (600), 29.6
10b	*c*	271–400 (58)	29 (600), 29.6

[a] The temperature range for major weight loss and the observed weight loss over this range. [b] The percent residue observed at the maximum temperature used (given in parentheses) and the calculated percent if the residue were pure platinum metal. [c] No melting transition observed.

The thermal properties of some of the model compounds and polymers have been studied by TGA and DSC (Table IV). While the model platinum(IV) complexes **2**, **7**, **8**, and **9** melt before the onset of decomposition, no melting was observed for the polymers **10a** and **10b**. However, the temperature at which decomposition began was similar for the models and polymers in the range 205–271 °C (Table IV), indicating that all such compounds have high thermal stability. Most of the platinum(IV) compounds underwent major weight loss in the temperature range 200–450 °C, but slow weight loss occurred at higher temperatures so that the weight loss associated with a residue of pure platinum was not obtained at the maximum temperatures studied (Table IV). However, the polymers **10a** and **10b** gave very similar thermal behaviors and the residue at 600 °C corresponded to formation of metallic platinum.

Experimental Section

^{1}H NMR spectra were recorded using Varian XL200 or Gemini 300 MHz spectrometers. FTIR spectra were recorded as KBr disks by using a Bruker IR/32 spectrometer. Thermal analyses were carried out by using a Perkin-Elmer DSC7 and TAC7/DX differential scanning calorimeter and thermogravimetric analyzer, respectively. The complexes $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ and $[PtMe_2(bpy)]$ were prepared as described previously.[13] The ligand bu$_2$bpy was prepared by reaction of 4-*tert*-butylpyridine with Raney nickel, by a modification of the known method.[14]

[PtMe$_2$(bu$_2$bpy)]. Solutions of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (0.50 g) in ether (25 mL) and bu$_2$bpy (0.47 g) in ether (15 mL) were mixed and allowed to stand for 1 day. The orange precipitate of the product was separated by filtration, washed with *n*-pentane, and dried under vacuum. Yield: 87%. Anal. Calcd for $C_{20}H_{30}N_2Pt$: C, 48.7; H, 6.1; N, 5.7. Found: C, 48.5; H, 5.9; N, 5.7. NMR in acetone-d_6: $\delta(^1H)$ = 0.91 [s, 6H, ^2J(PtH) = 86 Hz, *Me*Pt], 1.42 [s, 18H, *t*-Bu], 7.68 [dd, 2H, $^3J(H^5H^6)$ = 6 Hz, $^4J(H^3H^5)$ = 2 Hz, bpy-H^5], 8.44 [d, 2H, $^4J(H^3H^5)$ = 2 Hz, bpy-H^3], 9.07 [d, 2H, $^3J(H^5H^6)$ = 6, $^3J(PtH^6)$ = 22 Hz, bpy-H^6]; $\delta(^{195}Pt)$ = –197 (reference aqueous K_2PtCl_4).

[PtBrMe$_2$(CH$_2$CO$_2$Me)(bpy)]. To a solution of [PtMe$_2$(bpy)] (0.05 g) in acetone (10 mL) was added $BrCH_2CO_2Me$ (0.2 mL). The solution color immediately changed from orange to pale yellow. The solvent was evaporated under vacuum to give the product, which could be recrystallized from acetone. Yield: 85%. Anal. Calcd for $C_{15}H_{19}BrN_2O_2Pt$: C, 33.7; H, 3.6; N, 5.2. Found: C, 33.4; H, 3.6; N, 4.8. NMR in acetone-d_6: **2a**, $\delta(^1H)$ = 1.43 [s, 6H, ^2J(PtH) = 69 Hz, MePt], 2.01 [s, 2H, ^2J(PtH) = 96 Hz, PtCH$_2$], 2.67 [s, 3H, MeO], 7.84 [m, 2H, bpy-H^5], 8.29 [m, 2H, bpy-H^4], 8.67 [m, 2H, bpy-H^3], 8.82 [m, 2H, ^3J(PtH) = 17 Hz, bpy-H^6]. For resolved peaks of **2b**, see Table I. IR: ν(CO) = 1714 cm^{-1}. MS: *m/z* = 454 [parent P – Br]$^+$.

The following were similarly prepared. [PtBrMe$_2$(CH$_2$CO$_2$Et)(bpy)], **3**: yield 88%; NMR in acetone-d_6 (**3a**) $\delta(^1H)$ = 0.75 [t, 3H, ^3J(HH) = 7, *Me*CH$_2$], 1.44 [s, 6H, ^2J(PtH) = 69 Hz, MePt], 2.00 [s, 2H, ^2J(PtH) = 96 Hz, Pt*CH$_2$*], 2.99 [q, 2H, ^3J(HH) = 7 Hz, *CH$_2$*O], 7.80, 8.26, 8.62, and 8.80 [m, each 2H, bpy]; IR ν(CO) = 1703 cm^{-1}; MS: *m/z* = 547 [P]$^+$, 467 [P-Br]$^+$. Anal. Calcd for $C_{16}H_{21}N_2BrO_2Pt$: C, 35.0; H, 3.8; N, 5.1. Found: C, 35.2; H, 3.6; N, 4.8. [PtBrMe$_2$(CH$_2$CO$_2$H)(bpy)], **4**: yield 80%; NMR in acetone-d_6 (**4a**) $\delta(^1H)$ = 1.45 [s, 6H, ^2J(PtH) = 69 Hz, MePt], 1.99 [s, 2H, ^2J(PtH) = 97 Hz, Pt*CH$_2$*], 7.82, 8.26, 8.62, and 8.86 [m, each 2H, bpy]. Anal. Calcd for $C_{14}H_{17}N_2BrO_2Pt$: C, 32.3; H, 3.3; N, 5.4. Found: C, 32.4; H, 3.1; N, 5.3. [PtBrMe$_2$(CH$_2$CN)(bpy)], **5**: yield 78%; NMR in CD_2Cl_2 (**5a**) $\delta(^1H)$ = 1.48 [s, 6H, ^2J(PtH) = 69 Hz, MePt], 1.69 [s, 2H, ^2J(PtH) = 93 Hz, Pt*CH$_2$*], 7.74, 8.16, 8.32, and 8.84 [m, each 2H, bpy]; MS *m/z* = 501 [P]$^+$, 431 [P-2Me-CH$_2$CN], 421 [P-Br]$^+$. Anal. Calcd for $C_{14}H_{16}N_3BrPt$: C, 33.5; H, 3.2; N, 8.4. Found: C, 33.1; H, 2.9; N, 8.2. [PtBrMe$_2$(CH$_2$CONH$_2$)(bpy)], **6**: yield 90%; NMR in dmso-d_6 (**6a**) $\delta(^1H)$ = 1.31 [s, 6H, ^2J(PtH) = 69 Hz, MePt], 1.88 [s, 2H, ^2J(PtH) = 93 Hz, Pt*CH$_2$*], 5.70 and 6.26 [br s, each 1H, NH$_2$], 7.77, 8.22, and 8.7 [m, 2H, 2H, 4H respectively, bpy]; IR ν(CO) = 1655 cm^{-1}, ν(NH) = 3395, 3175 cm^{-1}; MS *m/z* = 520 [P]$^+$, 439 [P-Br]$^+$. Anal. Calcd for $C_{14}H_{18}N_3BrOPt$: C, 32.4; H, 3.5; N, 8.1. Found: C, 32.9; H, 3.4; N, 8.0. [PtBrMe$_2$(CH$_2$CO$_2$CH=CH$_2$)(bu$_2$bpy)], **7**: yield 67%; NMR in CD_2Cl_2 (**7a**) $\delta(^1H)$ = 1.45 [s, 18H, *t*-Bu], 1.47 [s, 6H, ^2J(PtH) = 68 Hz, MePt], 2.12 [s, 2H, ^2J(PtH) = 98 Hz, Pt*CH$_2$*], 4.14 [m, 2H, =CH$_2$], 6.34 [m, 1H, =CH], 7.62, 8.18 and 8.66 [m, each 2H, bpy]; IR ν(CO) = 1726 cm^{-1}. Anal. Calcd for $C_{24}H_{35}N_2BrO_2Pt$: C, 43.8; H, 5.3; N, 4.2. Found: C, 43.5; H, 5.0; N, 4.3.

[{PtBrMe$_2$(bpy)}$_2$(μ-CH$_2$CO$_2$CH$_2$CH$_2$O$_2$CCH$_2$)]. To a solution of [PtMe$_2$(bpy)] (0.10 g) in acetone (10 mL) was added $BrCH_2CO_2CH_2CH_2O_2CCH_2Br$ (0.04 g, prepared by transesterification of $BrCH_2CO_2Me$ (2 equiv) with $HOCH_2CH_2OH$ (1 equiv) using *p*-toluenesulfonic acid catalyst at 90 °C). The solution color changed from orange to yellow, and the product precipitated from solution; it was isolated by filtration, washed with ether, and dried under vacuum. Yield: 53%. Anal. Calcd for $C_{30}H_{36}N_4Br_2O_4Pt_2$: C, 33.8; H, 3.4; N, 5.2. Found: C, 33.9; H, 3.1; N, 5.3. NMR in CD_3CN: $\delta(^1H)$ = 1.40 [s, 12H, ^2J(PtH) = 69, MePt], 2.00 [s, 4H, ^2J(PtH) = 98, CH$_2$Pt], 2.79 [br s, 4H, CH$_2$O], 7.66, 8.16, 8.38, and 8.74 [m, each 4H, bpy]. MS: *m/z* = 986 [P – Br]$^+$.

Similarly was prepared [{PtBrMe$_2$(bu$_2$bpy)}$_2$(μ-CH$_2$CO$_2$CH$_2$CH$_2$O$_2$CCH$_2$)] as a pale yellow solid. Yield: 61%. Anal. Calcd for $C_{46}H_{68}N_4Br_2O_4Pt_2$: C, 42.8; H, 5.3; N, 4.3. Found: C, 42.2; H, 5.3; N, 4.0. NMR in CD_2Cl_2: $\delta(^1H)$ = 1.43 [s, 36H, *t*-Bu], 1.46 [s, 12H, ^2J(PtH) = 68, MePt], 2.07 [s, 4H, ^2J(PtH) = 99, CH$_2$Pt], 2.92 [br s, 4H, CH$_2$O], 7.61, 8.15, and 8.62 [m, each 4H, bpy]. IR: ν(CO) = 1707 cm^{-1}. MS: *m/z* = 1211 [P – Br]$^+$.

Polymerization of [PtBrMe$_2$(CH$_2$CO$_2$CH=CH$_2$)(bu$_2$bpy)]. A solution of [PtBrMe$_2$(CH$_2$CO$_2$CH=CH$_2$)(bu$_2$bpy)] (0.15 g) and dibenzoyl peroxide (0.02 g) in dry *t*-BuOH (10 mL) was degassed by several freeze–pump–thaw cycles at 10^{-4} Torr, then sealed under vacuum, and heated to 75 °C for 1 day. The solvent volume was reduced, and the product was precipitated with ether. Yield: 40%. Anal. Calcd for $(C_{24}H_{35}N_2BrO_2Pt)_n$: C, 43.8; H, 5.3; N, 4.2. Found: C, 44.8; H, 4.8; N, 3.2. NMR: see text. IR: ν(CO) = 1707 cm^{-1}.

Poly(vinyl bromoacetate). To a solution of poly(vinyl alcohol) (1.0 g, *M* = 50 000) in dry $MeCONMe_2$ (100 mL) was added $BrCH_2COBr$ (4 mL), and the mixture was stirred at room temperature for 2 h. The product was precipitated by addition of distilled water, then washed with dilute sodium carbonate solution and more distilled water, and dried under vacuum. Yield: 86%. Anal. Calcd for $(C_4H_5BrO_2)_n$: C, 29.1; H, 3.0. Found: C, 29.2; H, 2.8. NMR in CD_2Cl_2: $\delta(^1H)$ = 1.93 [br, 2H, CH$_2$], 3.9 [br s, 2H, CH$_2$Br], 4.95 [br, 1H, CHO]. IR: ν(CO) = 1734 cm^{-1}.

---

(13) (a) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1643. (b) Chaudhury, N.; Puddephatt, R. J. *J. Organomet. Chem.* **1975**, *84*, 105.

(14) Bager, G. M.; Sasse, W. H. F. *J. Chem. Soc.* **1956**, 616.

Table V. Crystallographic Data for 2a and 9a

compd, formula	**2a**, $C_{15}H_{19}BrN_2O_2Pt$	**9a**, $C_{46}H_{68}Br_2N_4O_4Pt_2 \cdot C_3H_6O$
fw	534.32	1349.15
cryst syst, space group	triclinic, $P\bar{1}$	monoclinic, *Cc*
cell dimens	10.279(2)	10.858(2)
a/Å	10.387(2)	25.730(4)
b/Å	8.994(2)	21.375(2)
α/deg	109.50(1)	90
β/deg	108.04(2)	100.69(1)
γ/deg	69.33(2)	90
temp/K	296	296
cell vol/Å^{-3}, *Z*	826.7(5), 2	5868.4(15), 4
dens/g·cm^{-3} (obsd, calcd)	2.11(5), 2.147	1.520(5), 1.527
F(000)	503.9	2583.6
radiation, wavelength/Å	Mo Kα, 0.710 73	Cu Kα, 1.541 84
abs coeff/cm^{-1}	109.7	101.0
no. of unique data	2904	4061
no. of observ, variables	2539 ($I \geq 2.5\sigma(I)$), 142	3303 ($I \geq 3\sigma(I)$), 282
final model (*R* and R_w)	0.0215, 0.0207	0.0556, 0.0672

Table VI. Positional (×10^4) and Thermal Parameters (×10^3) for 2a

atom	*x*	*y*	*z*	U_{eq}/Å^2 [a]
Pt	2644.5(2)	−2976.3(2)	2707.6(2)	37.8(1)*
Br	65.9(6)	−2031.9(6)	3074.4(7)	58.8(2)*
O(1)	5950(5)	−2071(5)	3455(6)	95(2)*
O(2)	5114(4)	−2776(4)	800(5)	66(2)*
N(1)	1902(4)	−3383(4)	109(4)	40(2)*
N(2)	2419(4)	−995(4)	2231(4)	39(2)*
C(1)	2775(6)	−4924(6)	2935(7)	64(3)*
C(2)	3401(6)	−2374(6)	5159(6)	60(2)*
C(3)	4739(5)	−3889(6)	2446(6)	52(2)*
C(4)	5345(5)	−2833(6)	2333(7)	54(2)*
C(5)	5591(8)	−1669(7)	657(10)	104(4)*
C(6)	1660(5)	−4603(6)	−903(6)	53(1)
C(7)	1296(6)	−4808(6)	−2555(7)	61(1)
C(8)	1143(6)	−3705(6)	−3173(7)	61(1)
C(9)	1339(5)	−2441(6)	−2170(6)	54(1)
C(10)	1727(5)	−2295(5)	−513(5)	38(1)
C(11)	1965(5)	−979(5)	658(5)	39(1)
C(12)	1729(5)	250(6)	185(6)	52(1)
C(13)	1957(6)	1451(6)	1347(7)	58(1)
C(14)	2431(6)	1435(6)	2919(7)	62(1)
C(15)	2653(5)	180(6)	3361(7)	55(1)

[a] Values with an asterisk refer to atoms that were refined anisotropically and are given in the form of the isotropic equivalent displacement parameter defined as $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*/\mathbf{a}_i\cdot\mathbf{a}_j$.

Table VII. Positional (×10^4) and Thermal (×10^3) Parameters for 9a

atom	*x*	*y*	*z*	U_{eq}/Å^2 [a]
Pt(1)	0	−1287.5(4)	0	60.6(3)*
Pt(2)	6144.7(15)	956.5(4)	−326.5(7)	64.8(4)*
Br(1)	−1997(3)	−1718(1)	160(2)	95(1)*
Br(2)	8089(3)	1223(1)	466(2)	89(1)*
N(1)	−35(17)	−830(8)	789(9)	53(5)
N(2)	1082(18)	−1718(7)	723(9)	56(5)
N(3)	5874(18)	322(8)	238(10)	60(5)
N(4)	5035(20)	1271(9)	255(11)	68(6)
C(1)	−623(26)	−331(11)	775(14)	73(7)
C(2)	−572(24)	−63(11)	1352(13)	68(7)
C(3)	−26(24)	−282(10)	1928(13)	67(6)
C(4)	545(23)	−761(10)	1909(13)	62(6)
C(5)	546(21)	−1024(9)	1356(11)	49(5)
C(6)	1128(23)	−1528(10)	1306(12)	59(6)
C(7)	1682(20)	−1807(9)	1852(11)	49(5)
C(8)	2262(24)	−2308(11)	1801(13)	70(7)
C(9)	2271(24)	−2458(10)	1174(12)	67(7)
C(10)	1561(26)	−2191(12)	664(15)	78(8)
C(11)	6326(27)	−158(12)	196(15)	78(8)
C(12)	6147(30)	−553(14)	582(16)	93(9)
C(13)	5533(25)	−462(11)	1140(13)	69(7)
C(14)	5070(25)	40(10)	1172(13)	69(7)
C(15)	5270(23)	424(10)	719(12)	61(6)
C(16)	4836(22)	951(9)	768(12)	57(6)
C(17)	4106(25)	1144(11)	1176(14)	69(7)
C(18)	3558(25)	1639(11)	1129(13)	69(7)
C(19)	3847(23)	1932(11)	619(12)	66(6)
C(20)	4524(25)	1738(11)	210(14)	67(7)
O(1)	2506(27)	−407(12)	620(15)	128(9)
O(2)	1206(22)	−46(8)	−207(11)	92(6)
O(3)	2974(20)	645(8)	−534(11)	89(6)
O(4)	2757(34)	1261(13)	−1225(17)	150(11)
C(21)	1503(27)	−928(12)	−259(16)	82(9)
C(22)	1821(32)	−457(14)	79(17)	93(9)
C(23)	1499(34)	468(14)	79(17)	97(10)
C(24)	1818(36)	806(15)	−384(20)	103(10)
C(25)	3427(37)	879(16)	−934(20)	106(11)
C(26)	4641(26)	711(13)	−1068(14)	78(8)
C(27)	114(51)	−1818(12)	−773(18)	126(13)*
C(28)	−1024(27)	−825(9)	−728(12)	65(8)*
C(29)	6280(30)	1650(12)	−891(17)	89(10)*
C(30)	7291(31)	588(13)	−863(18)	95(10)*
C(31)	87(24)	37(10)	2534(12)	83(8)
C(32)	−641(35)	554(13)	2432(23)	159(5)
C(33)	1477(23)	147(17)	2814(23)	159(5)
C(34)	−480(37)	−311(14)	2996(23)	159(5)
C(81)	2891(20)	−2591(9)	2385(10)	73(7)
C(82)	4244(25)	−2385(16)	2565(21)	159(5)
C(83)	2207(36)	−2515(17)	2949(18)	159(5)
C(84)	2913(40)	−3173(11)	2217(22)	159(5)
C(131)	5366(22)	−878(9)	1537(12)	76(7)
C(132)	4722(36)	−1334(15)	1135(20)	159(5)
C(133)	6674(25)	−1049(17)	1888(21)	159(5)
C(134)	4562(35)	−710(18)	2026(19)	159(5)
C(181)	2738(25)	1840(11)	1545(13)	111(11)
C(182)	1432(32)	1989(17)	1170(20)	159(5)
C(183)	2599(43)	1449(15)	2074(20)	159(5)
C(184)	3421(37)	2331(14)	1843(20)	159(5)
O(5)	−3997(48)	−875(21)	−1705(26)	146(14)
C(41)	−5107(48)	−752(21)	−1761(26)	146(14)
C(42)	−5781(48)	−844(21)	−1229(26)	146(14)
C(43)	−5749(48)	−488(21)	−2346(26)	146(14)
O(6)	−1450(81)	2802(31)	−1345(40)	125(16)
C(51)	−653(81)	2571(31)	−958(40)	125(16)
C(52)	−426(81)	2730(31)	−280(40)	125(16)
C(53)	−138(81)	2072(31)	−1141(40)	125(16)
O(6′)	−1294(80)	2970(33)	−509(38)	125(16)
C(51′)	−582(80)	2594(33)	−430(38)	125(16)
C(52′)	−387(80)	2281(33)	−985(38)	125(16)
C(53′)	201(80)	2497(33)	204(38)	125(16)

[a] Values with an asterisk refer to atoms that were refined anisotropically and are given in the form of the isotropic equivalent displacement parameter defined as $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$.

[PtMe$_2$(bu$_2$bpy)] with Poly(vinyl bromoacetate). Solutions of poly(vinyl bromoacetate) (0.046 g) in acetone (10 mL) and [PtMe$_2$(bu$_2$bpy)] (0.15 g) in acetone (10 mL) were mixed and stirred at room temperature. The color changed from orange to yellow, and the product polymer **10b** precipitated from solution. The solvent volume was reduced, and the product was separated and washed with pentane. Yield: 65%. Anal. Calcd for $(C_{24}H_{35}N_2BrO_2Pt)_n$: C, 43.8; H, 5.3; N, 4.2. Found: C, 43.0; H, 5.4; N, 3.9. NMR in CD_2Cl_2: ^1H, see text; $\delta(^2H)$ for **10b**-d_6 = 1.4 [br, CD_3Pt *trans* to N], 0.6 [br, CD_3Pt *trans* to Br]. IR: ν(CO) = 1701 cm^{-1}.

X-ray Structure Determination. Compounds **2a** and **9a** were examined by similar experimental procedures. An overview is given below, followed by details specific to each analysis. Crystallographic data are summarized in Table V.

Crystal densities were determined by the neutral buoyancy method in mixtures of bromoform and carbon tetrachloride for **2a** and 1,2-dibromoethane and carbon tetrachloride for **9a**. Light yellow crystals were mounted on glass fibers using epoxy resin in air for data collection. All the single crystal X-ray diffraction measurements were carried out by using an Enraf-Nonius CAD4F diffractometer at ambient temperature (296 K). Cell constants and orientation matrices were determined and refined by using the angular settings for 20 high angle reflections with 24.1 < 2θ

$< 31.8°$ for **2a** and 22 reflections with $52.6 < 2\theta < 57.6°$ for **9a**. Intensity data were recorded in the θ–2θ scan mode at variable scan speeds (1.37–3.30 for **2a** and 1.65–4.12 deg min^{-1} for **9a**), so chosen as to optimize counting statistics within a maximum time per datum of 60 s.[15] Background estimates were made by extending the scan by 25% on each side for **2a**, whereas static background measurements were made at the end points of the width $(1.5 + 0.14 \tan \theta)°$ for **9a**. Three standard reflections were monitored for every 180 min for **2a** and 120 min for **2a** of X-ray exposure time and showed only 0.4% variation in the intensity over 64.7 h for **2a** and 2.3% decline in 62.6 h for **9a**. Lorentz, polarization, and background radiation corrections were applied using the Structure Determination Package running on a PDP11/23+ computer.[16] A decay correction was applied to **9a**. Absorption corrections were applied to the data using the program AGNOST[17] for **2a** and ABSCOR[18] for **9a**. A p factor of 0.04 was applied[19] to the data for **9a**. Both the structures were solved by a combination of SHELXS-86 software[20] and difference Fourier techniques. Refinements were made by full-matrix least-squares techniques on F, using SHELX-76 software[21] running on a SUN3/80 workstation. Scattering factors for neutral non-hydrogen atoms were taken from ref 22.

The single crystals of **2a** were grown from acetone solution. For crystal **2a** (with dimensions 0.14 × 0.14 × 0.24 mm), intensities of 3264 reflections ($-12 \le h \le 12$, $-12 \le k \le 1$, $-10 \le l \le 10$; $0 < 2\theta < 50°$) and 25 repetitions of 3 standards were collected. Eight crystal faces were identified, and the distances between the faces were measured for the absorption correction. The intensity statistics computed using NZTEST[23] suggested the acentric space group $P1$, and the structure was readily solved. With Pt, Br, O, and C(1) to C(5) carbon atoms assigned anisotropic thermal parameters, refinement converged at $R = 0.0205$. At this stage it became apparent that the two unique molecules were related by a center of symmetry. Accordingly, the symmetry equivalent reflections were averaged, $R_f = 0.007$ to give 2904 unique data with $I \ge 2.5\sigma$, and refinement was completed in the space group $P\bar{1}$, No. 2. Anisotropic thermal parameters were assigned for Pt, Br, C(1), C(2), C(3), C(4), C(5), and all the O atoms. All 19 hydrogen atoms were successfully located by difference Fourier methods with electron densities in the range 0.876–0.485 e Å^{-3}. The hydrogen atoms were placed in the idealized positions (C–H = 0.95 Å) and were included for structure factor calculations only. A common temperature factor was assigned to all hydrogen atoms and was refined. With the use of 2539 ($I \ge 2.5\sigma(I)$) observations, and 142 parameters, the model converged at agreement factors $R = 0.0215$, $R_w = 0.0207$ (using the weighting scheme of the form $w = k/\sigma^2(F_o) + gF^2$ where $k = 1.8481$ and $g = 0.000\,079$).

Single crystals of **9a** were grown by the diffusion of pentane into an acetone solution at room temperature. Intensities from 4195 data were recorded ($-11 \le h \le 11$, $-1 \le k \le 27$, $-1 \le l \le 22$; $0 < 2\theta < 110°$), along with 40 repetitions of the three standards. The data crystal had nine faces, all of which were indexed, and the distances between them were measured for absorption correction. The cell parameters and the systematic absences (hkl, $h + k = 2n + 1$, $h0l$, $h,l = 2n + 1$, $0kl$, $k = 2n + 1$, $hk0$, $h + k = 2n + 1$, $0k0$, $k = 2n + 1$, $h00$, $h = 2n + 1$, $00l$, $l = 2n + 1$) suggested that the space group was either Cc (No. 9) or $C2/c$ (No. 15),[22] and a zero-moment test[23] strongly indicated the noncentrosymmetric space group. The data were averaged for the space group Cc; $R_f = 0.014$ (0.024 for $C2/c$) to give 4061 independent reflections. The correct choice of the space group was confirmed by successful solution and refinement of the structure. The program MISSYM[24] indicated the absence of any additional symmetry. Anisotropic thermal parameters were assigned for Pt, Br, and the methyl C atoms attached to the Pt atoms and refined. Unreasonably large thermal parameters and C–C distances were found for the methyl carbon atoms of the *tert*-butyl groups. The C–C bond distance was fixed (C–C = 1.542 Å), and a common thermal parameter was refined in the least-squares refinements. The solvent molecule acetone was located. The disorder present in half of the molecule was successfully resolved. For the non-hydrogen atoms present in the acetone, a common temperature factor was assigned and refined. No hydrogen atoms were included for the solvent molecule or for the methyl carbon atoms of the *tert*-butyl groups. The hydrogen atoms were included in their idealized positions (with a fixed $U = 0.10$ Å^2) for the rest of the molecule for the purpose of the structure factor calculations only. With the use of 3303 ($I \ge 3\sigma(I)$) observations and 282 variables, the refinement (on F^2) converged at agreement factors $R = 0.0556$ and $R_w = 0.0672$, utilizing weights of the form $w = k/\sigma^2(F_o) + gF^2$ where $k = 0.0326$ and $g = 0.110\,636$. For the inverted model, $R = 5.71\%$ and $R_w = 6.74\%$. The experimental details and crystal data and the positional and U(eq) thermal parameters for **2a** and **9a** are given in Tables V–VII. Tables of anisotropic thermal parameters, calculated hydrogen atom positions, root-mean-square amplitudes of vibration, and weighted least-squares planes and dihedral angles have been deposited.

Acknowledgment. We thank NSERC (Canada) for financial support and Dr. N. C. Payne for access to X-ray facilities.

Supplementary Material Available: Tables of anisotropic thermal parameters, calculated hydrogen atom positions, root-mean-square amplitudes of vibration, weighted least-squares planes and dihedral angles, and torsion angles (9 pages). Ordering information is given on any current masthead page.

OM930418O

---

(15) *Enraf-Nonius CADF Users Manual*; Enraf-Nonius: Delft, The Netherlands, 1988.

(16) "Enraf-Nonius Structure Determination Package", SDP-PLUS, Version 3.0, 1985.

(17) Cahen, D.; Ibers, J. A. *J. Appl. Crystallogr.* **1972**, *5*, 298.

(18) Coppens, P.; Leiserowitz, L.; Rabinovich, D. *Acta Crystallogr.* **1968**, *18*, 1035.

(19) Busing, W. R.; Levy, H. A. *J. Chem. Phys.* **1957**, *26*, 563.

(20) Sheldrick, G. M. SHELXS-86, Structure Solving Program. University of Gottingen, FDR, 1986.

(21) Sheldrick, G. M. SHELX-76, Program for Crystal Structure Determination. University of Cambridge, England, 1976.

(22) *International Tables for X-ray Crystallography*: (a) Kynoch Press: Birmingham, England, 1974; Vol. 4. (b) D. Reidel Publishing Co.: Boston, 1983; Vol. A.

(23) Howells, E. R.; Phillips, D. C.; Rogers, D. *Acta Crystallogr.* **1950**, *3*, 210.

(24) Le Page, Y. *Acta Crystallogr.* **1987**, *20*, 264.