as follows (the energy differences between the Rb and Cs spectra are in parentheses, and all data are in cm^{-1}): 16 800 (370), 19 600 (280), 23 590 (350), 30 230 (900), and 33 610 (790). This indicates that the complexes are isomorphous, but that the different sizes of the 8-coordinated Rb$^+$ (1.75 Å) and Cs$^+$ (1.88 Å)[9] cause small differences in bond lengths in the chromophore together with a slightly stronger ligand field in the Rb compound.

IR Spectra. The bands which appear in the IR spectra (4000–35 cm^{-1}) of $Cs_3VCl_6{\cdot}4H_2O$ and related compounds are listed in Table III. Substitutions of Rb for Cs, Br for Cl, and D_2O for H_2O were made to make assignments more feasible. Since the chromophore has D_{4h} symmetry, the IR active bands belong to the a_{2u} and e_u representations. Of the bands below 1000 cm^{-1}, the former are ν(V–Cl), VO_4 (out-of-plane bend), and H_2O (rocking), and the latter are $\nu(V{-}OH_2)$, VO_4 (in-plane bend), ClVCl bend, and H_2O (wagging).

The bands ~3200, 1653, and 1620 cm^{-1} shift on deuteration and are clearly the H_2O stretching (a_{2u} and e_u) and bending (e_u) vibrations. The splitting of the latter band may be due to the fact that the H_2O molecules are strongly H bonded to the Cl^- in the lattice and the whole array should be considered in determining the selection rules. The bands at 740 and 610 cm^{-1} also shift markedly upon deuteration and are assigned to the H_2O wag and rock, respectively. This is the order suggested by Adams and Lock;[19] it is an inversion of the usual order proposed. In the deuterated compound these bands are much weakened, but the exact position of the D_2O bands is not very clear in the spectrum.

For hexahydrates of trivalent metals the IR active $\nu(M{-}OH_2)$ (ν_3) falls in the range 540–488 cm^{-1}.[20] This is the basis for the assignment of the strong band at 511 cm^{-1} in the chloro complex. The reason for the slight splitting in this band is not clear, but it may again be related to the strong H bonding of the $V(OH_2)_4$ group with eight Cl^- in the lattice. The band at 356 cm^{-1} shifts to 311 cm^{-1} on bromination. In $TiX_3{\cdot}6H_2O$ (X = Cl, Br), which most likely contain the *trans*-$[TiX_2(H_2O)_4]^+$ chromophores, bands at 336 (Cl) and 294 (Br) have been assigned to the titanium–halogen stretch.[21]

Without the introduction of factor-group analysis, one expects only three more IR-active low-frequency vibrations: $\delta(VO_4$ out-of-plane) a_{2u}, $\delta(VO_4$ in-plane) e_u, and δ(Cl–V–Cl) e_u. A *probable* assignment of these three is given in Table III. This is the same ordering given for $TiX_3{\cdot}6H_2O$.[21] The band at 239 cm^{-1} in the Cl^- complex is quite sensitive to deuteration and so may more probably represent out-of-plane motion of the VO_4 group. It should be remembered that in the crystal the waters tend to be held perpendicular to the VO_4 plane by H bonding. The X–V–X bend would be expected to lie below the VO_4 bends because of the greater masses of the halogens over oxygen. The above assignments agree with those given by Podmore and Smith[3] for $Cs_2VCl_5{\cdot}4H_2O$ and $Cs_2VBr_5{\cdot}5H_2O$.

All four vibrations in the range 195–360 cm^{-1} are lowered by substitution of Br for Cl, despite the assignment of two of them to $\delta(VO_4)$ vibrations. One of these latter has the same symmetry as the V–X stretch (a_{2u}) and the other the same as the X–V–X bend (e_u). Mixing of vibrations of the same symmetry could cause all four vibrations to be sensitive to halogen substitution.

This analysis would assign all vibrations below 150 cm^{-1} to vibrations involving O–H···Cl bonding and to lattice modes. Clearly some of these assignments are quite tentative, and full confirmation of them could be made only if normal coordinate analysis were carried out. Adams[22] has noted several things about the bands in this range: (1) they fall in the same region as metal–halogen bends and so can be difficult to separate from them; (2) they can, if they possess the correct symmetry, mix with and perturb nearby internal modes of the same symmetry; (3) they can be distinguished by their dependence on mass. Thus, when the counterion is changed (here Cs → Rb), the internal frequencies should remain the same while the lattice modes change. In the present case, the three lowest bands will be clearly lattice modes since they rise in energy when Rb$^+$ is substituted for Cs$^+$.

Acknowledgment. P.J.M. acknowledges a grant from Research Corp. for the purchase of the Displex cryogenic refrigerator. We are grateful to Professor K. Nakamoto for obtaining the infrared spectra, to Dr. R. Blessing for some preliminary work on the X-ray structure, and to Mr. J. Buccafusco for some of the analyses. Thanks are also due to Dr. Horst Goetz of the Technische Universität Berlin who supplied the computer program for Gaussian analysis.

Registry No. $Cs_3[VCl_2(H_2O)_4]Cl_4$, 76773-12-1; $Cs_3VCl_6{\cdot}4H_2O$, 70410-29-6; $Rb_3[VCl_2(H_2O)_4]Cl_4$, 76773-13-2; $Rb_3VCl_6{\cdot}4H_2O$, 76773-14-3; $Cs_2[VBr_2(H_2O)_4]Br_3$, 39710-53-7; $Cs_2VBr_5{\cdot}4H_2O$, 76773-15-4; *trans*-$FeCl_2(H_2O)_4^+$, 53152-46-8; deuterium, 7782-39-0.

Supplementary Material Available: A listing of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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C,O-Chelates of the Trifluoroacetylacetonate Dianion with Platinum(II): Structure Assignment by means of ^{1}H, ^{13}C, ^{19}F, ^{31}P, and ^{195}Pt NMR Spectroscopy

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Bis(trifluoroacetylacetonato)platinum(II) reacted with triphenylphosphine, tris(*p*-chlorophenyl)phosphine, and triphenylarsine in diethyl ether or chloroform at room temperature to afford the [Pt(tfac(2–)-*C*,*O*)L_2] complexes. C,O-Chelation of the trifluoroacetylacetonate dianion in these complexes was confirmed by elemental analysis, molecular weight determination, IR and ^{1}H, ^{13}C, ^{19}F, ^{31}P, and ^{195}Pt NMR spectroscopy.

Acetylacetone and other β-dicarbonyl compounds are very versatile ligands[2] exhibiting various modes of bonding to metal ions as a neutral molecule[3] and a monoanion.[4] However compounds of the dianions are rather few, and only the selenium, tellurium, and phosphorus compounds have been reported so far. Thus $[Se_2(C_5H_6O_2)_2]$, $[Te(C_5H_6O_2)]$, and $[TeCl_2(C_5H_6O_2)]$ were identified by means of IR and ^1H NMR spectroscopy to have the tetraacetyldiselenacyclobutane and telluracyclohexane-3,5-dione structures, respectively,[5] and the C,C-chelate structures of the Te(II) and Te(IV) compounds have been confirmed by X-ray analysis.[6] On the other hand, the acetylacetonate dianion in $[(\eta^5\text{-}C_5H_5)Mn(CO)_2PPh(C_5H_6O_2)]$ was found to chelate the phosphorus atom as a *cis*-dienediolate.[7]

Recently we have been trying to explore the coordination chemistry of dianions of the β-dicarbonyl compounds and found novel linkage modes of the acetylacetonate dianion such as C,O,O-bridging between palladium(II) and another metal ion[8] and η-allylic coordination to palladium(II).[9] The present paper reports on C,O-chelation of the trifluoroacetylacetonate dianion, tfac(2−), to platinum(II).

Experimental Section

The starting chelates *cis*- and *trans*-[Pt(tfac)$_2$] were prepared by the method we had reported.[10] Commercial triphenylphosphine, tris(*p*-chlorophenyl)phosphine, and triphenylarsine were used without further purification.

[Pt(tfac(2−)-*C,O*)(PPh$_3$)$_2$] (1). (1) Triphenylphosphine (235 mg, 0.896 mmol) was added to a solution of *cis*-[Pt(tfac)$_2$] (191 mg, 0.381 mmol) in dry diethyl ether (10 mL) with stirring at room temperature. The solution became turbid at first and then deposited a colorless and transparent oily substance on the wall of the reaction vessel. On standing for about 1 h, the oil turned via a resinous substacne to tiny crystals, while the color of the solution changed from yellow to orange-red. The product was filtered and washed several times each with diethyl ether followed by ethanol and dried in vacuo. On standing, the filtrate deposited another crop of crystals. The total yield of [Pt(tfac(2−)-*C,O*)(PPh$_3$)$_2$]·$^1/_2$Et$_2$O was 186 mg (54%). Anal. Calcd for $C_{43}H_{38}O_{2.5}P_2F_3Pt$: C, 56.83; H, 4.21. Found: C, 56.38; H, 4.30.

The crude product, without washing, was dissolved in a minimum amount of dichloromethane, to which petroleum ether (bp 50 °C) was added drop by drop until the solution began to be turbid. The mixture was cooled with ice to deposit pale Naples-yellow crystallites of [Pt(tfac(2−)-*C,O*)(PPh$_3$)$_2$]·$^1/_4$CH$_2$Cl$_2$ in a 55% yield, which decomposed at 230–231 °C. Anal. Calcd for $C_{41.25}H_{33.5}O_2P_2F_3Cl_{0.5}Pt$: C, 55.48; H, 3.78; mol wt, 893. Found: C, 55.46; H, 3.87; mol wt, 896 in CH$_2$Cl$_2$.

Solvent-free crystals were obtained as white plates by recrystallizing the former product containing diethyl ether from an acetone solution on dropwise addition of petroleum ether; dec pt 238–240 °C. Anal. Calcd for $C_{41}H_{33}O_2P_2F_3Pt$: C, 56.49; H, 3.82. Found: C, 56.53; H, 3.82.

(2) Triphenylphosphine (209 mg, 0.767 mmol) was added to a solution of *trans*-[Pt(tfac)$_2$] (187 mg, 0.373 mmol) in a mixture of diethyl ether (20 mL) and dichloromethane (ca. 2 mL), and the mixture was left standing for 20 min at room temperature to precipitate a pale Naples-yellow powder. After filtration and washing with diethyl ether and ethanol successively, 197 mg of [Pt(tfac(2−)-*C,O*)(PPh$_3$)$_2$]·$^1/_2$Et$_2$O was obtained (58% yield), which was identical with the product from *cis*-[Pt(tfac)$_2$], giving the same IR and ^1H NMR spectra.

[Pt(tfac(2−)-*C,O*)[P(*p*-ClC$_6$H$_4$)$_3$]$_2$] (2). Tris(*p*-chlorophenyl)phosphine (109 mg, 0.30 mmol) and [Pt(tfac)$_2$] (72 mg, 0.14 mmol) were dissolved in chloroform (0.5 mL), and the mixture was left standing for 1 day at room temp. to deposit a yellow crystalline solid (119 mg). On recrystallizing from dichloromethane by addition of hexane drop by drop, pale yellow plates of [Pt(tfac(2−)-*C,O*)[P(*p*-ClC$_6$H$_4$)$_3$]$_2$] were obtained in a 39% yield (60 mg); dec pt 228–229 °C. Anal. Calcd for $C_{41}H_{27}O_2P_2F_3Cl_6Pt$: C, 45.66; H, 2.52. Found: C, 45.84; H, 2.52.

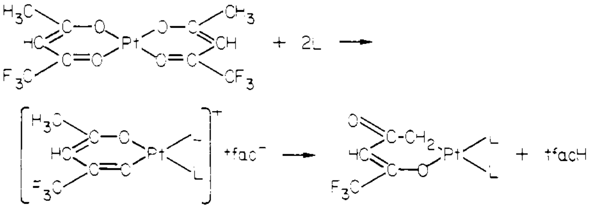
[Pt(tfac(2−)-*C,O*)(AsPh$_3$)$_2$] (3). Triphenylarsine (202 mg, 0.66 mmol) was reacted with *cis*-[Pt(tfac)$_2$] (109 mg, 0.217 mmol) in dry diethyl ether (2 mL) at room temp. until the solvent evaporated spontaneously to leave yellow needles. The crystals were washed with a mixture of diethyl ether and petroleum ether (1:2 by volume). The yield of [Pt(tfac(2−)-*C,O*)(AsPh$_3$)$_2$]·$^1/_2$Et$_2$O was 187 mg (87%). Anal. Calcd for $C_{43}H_{38}O_{2.5}As_2F_3Pt$: C, 51.82; H, 3.84. Found: C, 52.04; H, 3.95. *trans*-[Pt(tfac)$_2$] also gave the same product.

Recrystallization from dichloromethane on addition of petroleum ether gave yellow needles of [Pt(tfac(2−)-*C,O*)(AsPh$_3$)$_2$]·$^1/_4$CH$_2$Cl$_2$ in an overall yield of 71%; dec pt 222–223 °C. Anal. Calcd for $C_{41.25}H_{33.5}O_2As_2F_3Cl_{0.5}Pt$: C, 50.51; H, 3.44; mol wt, 981. Found: C, 50.89; H, 3.54; mol wt. 968 in CH$_2$Cl$_2$.

Measurements. Infrared spectra were obtained with a Hitachi 295 infrared spectrophotometer. Proton NMR spectra were recorded on JEOL C60-HL and PS100 instruments and ^{13}C NMR spectra on an FX-100 instrument by using Me$_4$Si as an internal reference in each case. ^{19}F, ^{31}P, and ^{195}Pt NMR spectra were measured by means of an FX-100 spectrometer with tunable probes. Molecular weight was determined with a vapor pressure osmometer manufactured by Knauer, Berlin, Germany.

Results and Discussion

Bis(trifluoroacetylacetonato)platinum(II) readily reacted with triphenylphosphine, tris(*p*-chlorophenyl)phosphine, and triphenylarsine to afford the [Pt(tfac(2−))L$_2$] complexes. The geometrical structure of the starting bischelate made no appreciable difference. The mechanism of reaction is not clear at the present stage of investigation, but the overall reaction may be presumed to proceed via the steps shown in eq 1 since



(1)

L = PPh$_3$ (1),
P(*p*-ClC$_6$H$_4$)$_3$ (2),
or AsPh$_3$ (3)

the trifluoroacetylacetonate ligand is readily displaced by bases such as dimethylphenylphosphine and 1,2-bis(diphenylphosphino)ethane to yield the outer-sphere complex [PtL$_4$](tfac)$_2$.[11] These products are mononuclear in dichloromethane, and the proposed C,O-chelated structure is reconciled with the following IR and NMR data.

Infrared spectra in Nujol show two or three strong bands in the 1500–1700 cm^{-1} region: **1**, 1620 vs. 1597 s; **2**, 1610 vs, 1595 vs, 1570 s; **3**, 1624 s, 1600 vs. The higher frequency band for each complex can be assigned to the ν(C=O) vibration, the frequency being reduced by ca. 160 cm^{-1} as compared with that for the keto tautomer of uncoordinated trifluoroacetylacetone (1785 cm^{-1}). Lowering of the ν(C=O) frequency may

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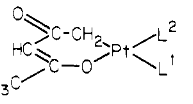
Table I. ^{1}H NMR Data in $CDCl_3$ at 27 °C: Chemical Shifts (Ppm) from Internal Me_4Si and Coupling Constants (Hz)[a]



L = PPh_3 (**1**), $P(p\text{-}ClC_6H_4)_3$ (**2**), or $AsPh_3$ (**3**)

complex	CH_2	CH	Ph
1	2.78 dds (^2J(Pt–H) = 53.5, ^3J(P^1–H) = 10, ^3J(P^2–H) = 5.5)	5.08 s	~7.2 m
2	2.76 dds (^2J(Pt–H) = 55, ^3J(P^1–H) = 10, ^3J(P^2–H) = 6)	5.14 s	~7.3 m
3	3.05 ss (^2J(Pt–H) = 60)	5.18 s	~7.2 m

[a] Key: s, singlet; ss, singlet with ^{195}Pt satellites; dds, double doublets with ^{195}Pt satellites; m, multiplet,

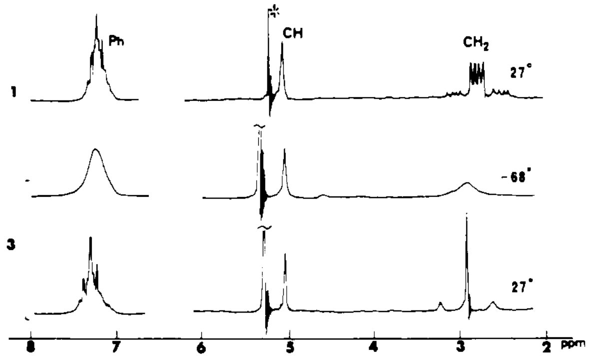


Figure 1. Proton NMR spectra at 100 MHz of [Pt(tfac(2–)-*C*,*O*)$(PPh_3)_2$]·$^1/_4CH_2Cl_2$ in $CDCl_3$ and [Pt(tfac(2–)-*C*,*O*)$(AsPh_3)_2$]·$^1/_4CH_2Cl_2$ in CD_2Cl_2, with Me_4Si as an internal reference. The peak marked with an asterisk is due to the solvent of crystallization, and the peak for the phenyl protons is reduced to one-tenth in area.

be caused by the electron-releasing effect of platinum bonded to the carbon atom neighboring the carbonyl group. The ν(C=O) bands of [PtX(CH_3)(1,2-bis(diphenylphosphino)ethane)] were observed at 1630 cm^{-1} for X = CH_2COCH_3 and at 1642 and 1627 cm^{-1} for X = $CH(COCH_3)_2$.[12] Analogous palladium(II) complexes also showed similar trends, the central-carbon-bonded acetylacetonate ligand in [Pd(acac)(acac-C^3)PPh_3][13] exhibiting the ν(C=O) band at 1665 vs and 1632 s cm^{-1}. These ν(C=O) frequencies for the carbon-bonded acetylacetonate ligand are 50–70 cm^{-1} lower than that for the keto tautomer of uncoordinated acetylacetone.[14]

The ^{1}H NMR data in $CDCl_3$ are listed in Table I and spectra of **1** and **3** are displayed in Figure 1. Three kinds of signals are observed at about 3, 5, and 7 ppm with the relative intensities of 2 : 1 : ca. 30 and are assigned to the methylene, methine, and phenyl protons. The methylene protons of the phosphine complexes **1** and **2** exhibit four-line signals of equal intensity flanked by the ^{195}Pt satellites. The separations among these signals are the same for both the 60- and 100-MHz spectra and are considered to be caused by coupling to the two nonequivalent phosphorus atoms. The methylene protons of complex **3** resonate as a singlet with ^{195}Pt satellites. As is seen in Figure 1, the spectrum of **3** in CD_2Cl_2 at −68 °C shows a marked broadening of the methylene signals. The six-membered chelate ring is not planar and the environment of the two methylene protons will be different when rapid conformational equilibration is hindered at lower temperatures. The values of ^2J(Pt–H) in Table I are comparable with those reported for *cis*-[PtX(CH_3)$(PEt_3)_2$] (52.2–59.4 Hz)[15] and [PtX(CH_3)(dppe)] (48.5–64.0 Hz)[12] with various anions as X and also with those for [Pt(CH_3)L(diars)]PF_6 (59.0–66.0 Hz)[16] where L is a neutral ligand and diars is *o*-phenylenebis(dimethylarsine). On the other hand the methine signal does not show coupling to ^{195}Pt, although ^4J(Pt–H) = ca. 11 Hz was observed for the methine proton in *cis*- and *trans*-[Pt$(tfac)_2$].[10]

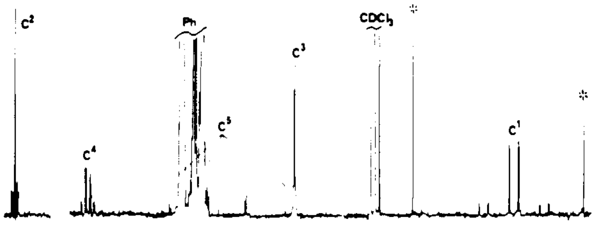


Figure 2. Carbon-13 NMR spectrum at 25.05 MHz of [Pt(tfac(2–)-*C*,*O*)$(PPh_3)_2$]·$^1/_2Et_2O$ in $CDCl_3$, with Me_4Si as an internal reference. Peaks marked with asterisks are due to the solvent of crystallization.

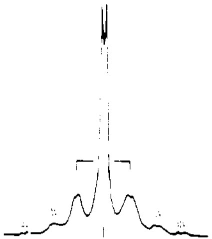


Figure 3. Fluorine-19 NMR spectrum at 93.66 MHz of [Pt(tfac(2–)-*C*,*O*)$(PPh_3)_2$]·$^1/_2Et_2O$ in $CDCl_3$, with C_6F_6 as an external reference. Asterisks denote the unidentified signals.

The ^{13}C NMR data are collected in Table II and the spectrum of **1** is shown in Figure 2 as an example. The C^1 atom exhibits a doublet of doublets in the case of **1** and **2** owing to the coupling to the two nonequivalent ^{31}P atoms, whereas C^1 of **3** resonates as a singlet. In each case ^{195}Pt satellites are observed, and the ^1J(Pt–C^1) value for **3** is larger than the values for **1** and **2**, reflecting the weaker trans influence of triphenylarsine than that of phosphines.[17] The ^1J(Pt–C^1) values of the present complexes (448–503 Hz) are appreciably smaller than ^1J(Pt–C) for *cis*-[Pt$(CH_3)_2L_2$] with a neutral ligand as L (590–690 Hz)[18] but are near those for [Pt(CH_3)L(diars)]PF_6 (453–575 Hz).[16] Although ^1J(Pt–C) for [Pt(acac)(acac-C^3)(py)] was 619 Hz, that for *trans*-[Pt(acac-C^3)$_2$$(py)_2$] was 369 Hz,[19] and the present values are between these two values.

The chemical shifts (204–205 ppm) and the small ^2J(Pt–C^2) values (46–54 Hz) of C^2 are reasonable for the uncoordinated carbonyl carbon, whereas C^2 in a η^3-acetylacetonato(2–) complex [Pt(acac(2–)-C^1–C^3)[P(p-ClC_6H_4)$_3$]$_2$] resonates at 177.8 ppm with *J*(Pt–C) = 168 Hz.[20] The signal for C^3 of **1** is split probably due to coupling to fluorine atoms, although the quartet structure is not clearly discernible. The signals

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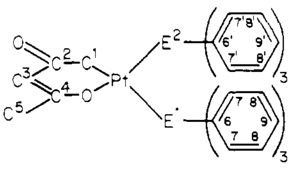
Table II. Proton-Decoupled Carbon-13 NMR Data from 20 000 Scans in $CDCl_3$ at 27 °C: Chemical Shifts (Ppm) from Internal Me_4Si and Coupling Constants (Hz)[a]



E = P for **1** and **2**
E = As for **3**

complex		C^1	C^2	C^3	C^4	C^5	$C^6, C^{6'}$	$C^7, C^{7'}$	$C^8, C^{8'}$	$C^9, C^{9'}$
1	δ	35.9 dds	205.4 ds	100.8 q	162.6 dq	121.1 dq	129.3 d 129.3 d	134.2 d 134.2 d	128.0 d 128.0 d	130.1 d 130.8 d
	J(Pt–C)	449	46							
	$J(P^1–C)$	72	3				64	12	13	3
	$J(P^2–C)$	4			4	10	64	12	10	3
	J(F–C)			~3	32	279				
2	δ	36.0 dds	204.4	101.4 br	162.3 dq	*b*	*c*	135.1 d	128.8 d	*c*
	J(Pt–C)	448	48							
	$J(P^1–C)$	71	4					12	12	
	$J(P^2–C)$	4			4			12	12	
	J(F–C)				32					
3	δ	27.7 ss	204.3 ss	101.2 br	162.9 q	126.3 q	130.3 s 132.3 s	133.3 s 133.6 s	128.5 s 128.8 s	129.8 s 130.6 s
	J(Pt–C)	503	54							
	J(F–C)				32	281				

[a] Key: ds, doublet with ^{195}Pt satellites; q, quartet; dq, double quartets; d, doublet; br, broad. [b] Indiscernible. [c] Complex.

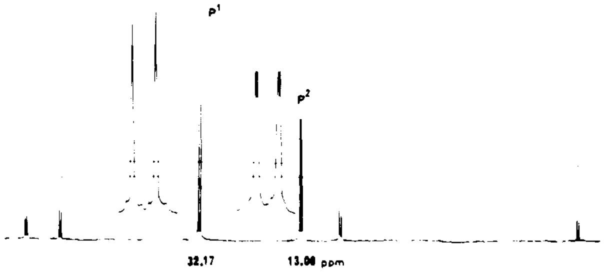
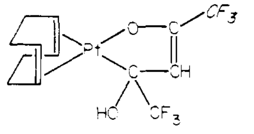


Figure 4. Phosphorus-31 NMR spectrum at 40.32 MHz of [Pt(tfac(2−)-*C,O*)$(PPh_3)_2$]·$^1/_2Et_2O$ in $CDCl_3$, with H_3PO_4 as an external reference.

for C^3 of **2** and **3** are both broad, but those for C^4 and C^5 of each complex are quartets except the C^5 signal from **2**, which is indiscernible due to poor solubility. Although the intensities of C^4 and C^5 resonances are rather low and ^{195}Pt satellites for these carbons are not detected, the coupling of C^4 and C^5 atoms to ^{31}P conforms with the O-bonding of the ligand to Pt(II), and the rather large chemical shift of C^4 as a vinyl ether carbon may be caused by the electron-attracting effect of the CF_3 group.

The ^{19}F, ^{31}P, and ^{195}Pt NMR spectra of **1** are shown in Figures 3, 4, and 5, respectively, and the data are collected in Table III together with those for **2** and **3**. The ^{19}F signal is a singlet for **3** and a doublet for **1** and **2** due to coupling to P^2, both types being flanked by ^{195}Pt satellites. The spectral data are similar to those for *cis*- and *trans*-[Pt(tfac)$_2$]; δ_F = 93.1 for cis and 93.0 for trans both with ^4J(Pt–F) = 18 Hz.[10] The ^{19}F atoms of the italic CF_3 group in **4**, which was prepared by the reaction of [Pt(COD)$_2$] with hexafluoroacetylacetone, were reported to resonate at 82.6 ppm, relative to the external C_6F_6, with ^4J(Pt–F) = 14.9 Hz.[21]



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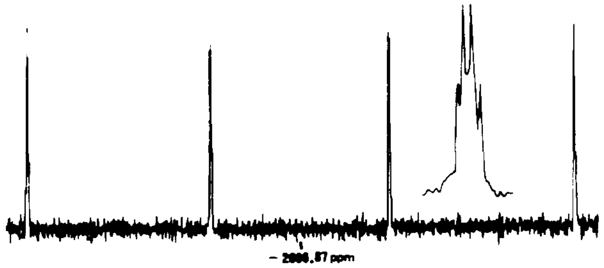

Figure 5. Platinum-195 NMR spectrum at 21.32 MHz of [Pt(tfac(2−)-*C,O*)$(PPh_3)_2$]·$^1/_2Et_2O$ in $CDCl_3$, with $K_2[PtCl_6]$ as an external reference.

Table III. ^{19}F, ^{31}P, and ^{195}Pt NMR Data from 40, 100, and 4000 Scans in $CDCl_3$ at 27 °C: Chemical Shifts (Ppm) and Coupling Constants (Hz)

	complex	δ_F[a]	^4J(Pt–F)	^5J(F–P)
^{19}F	1	93.16 ds	11.4	1.1
	2	92.75 ds	10.3	0.9
	3	92.56 ss	~9	

	complex	δ_P[b]	^1J(Pt–P)	^2J(P–P)	^5J(F–P)
^{31}P	1	32.17 ds (P^1)	2132.6	14.9	
		13.08 dqs (P^2)	4200.4	14.9	1.2
	2	31.00 ds (P^1)	2110.4	13.9	
		12.07 dqs (P^2)	4189	13.9	1.2

	complex	δ_{Pt}[c]	$^1J(Pt–P^1)$	$^1J(Pt–P^2)$	^4J(Pt–F)
^{195}Pt	1	−2606.87 ddq	2133.8	4198.0	11.0
	2	−2610.2 dd, br	2110	4188	
	3	−2593.9 s, br			

[a] Downfield positive from external C_6F_6. [b] Downfield positive from external H_3PO_4. [c] Downfield positive from external $K_2[PtCl_4]$.

As is seen in Figure 4, the two ^{31}P atoms in **1** are not equivalent but show separate signals coupling to each other.

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[21] The chemical shift was recalculated by use of δ_{CFCl_3} = 164.96 from the original value recorded by: Green, M.; Grove, D. M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 2228.

The higher field one with larger coupling to ^{195}Pt is assigned to P^2 trans to oxygen, which exerts a weaker trans influence than the carbon atom. Splitting of this signal due to coupling to ^{19}F also conforms to this assignment. The expected quartet structure is not so certain, but the $^5J(F-P^2)$ value of 1.2 Hz coincides well with 1.1 Hz observed in the ^{19}F spectrum.

The ^{195}Pt NMR spectrum in Figure 5 is composed of double doublets of quartets in accordance with the proposed structure. The coupling constants to ^{31}P and ^{19}F nuclei coincide exactly with those obtained from respective NMR spectra. In the case of **2** and **3**, on the other hand, the expected quartet structure due to coupling to ^{19}F is not observed, but the signal for **2** appears as double doublets and that for **3** as a singlet, both being broad.[22]

Acknowledgment. We are grateful to Mr. J. Gohda for the elemental analysis and also to the Ministry of Education, Japan, for a grant-in-aid (Grant No. 243014).

Registry No. **1**, 67560-32-1; **2**, 76705-35-6; **3**, 67560-33-2; *cis*-[Pt(tfac)$_2$], 67596-99-0; *trans*-[Pt(tfac)$_2$], 76740-70-0.

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(22) Very recently we have succeeded in preparing several palladium(II) complexes containing the trifluoroacetylacetonate dianion, of which the C,O-chelate structure was confirmed by X-ray analysis of [Pd(tfac-(2−)-*C,O*)PPh$_3$(2,6-Me$_2$-py)]: Kanehisa, N.; Miki, K.; Kasai, N.; Matsumoto, S.; Kawaguchi, S.; Okeya, S. 27th Symposium on Organometallic Chemistry in Japan, Tokyo, 1980; Abstracts, p 73.

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Structural Studies on Polynuclear Osmium Carbonyl Hydrides. 17.[1] $(\mu\text{-}H)Os_3(CO)_{10}[\mu\text{-}N{=}N(p\text{-tol})]$

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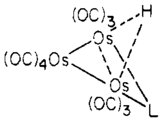
A single-crystal X-ray structural analysis has been performed on the complex $(\mu\text{-}H)Os_3(CO)_{10}[\mu\text{-}N{=}N(p\text{-tol})]$. This compound crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with a = 9.401 (2) Å, b = 13.463 (4) Å, c = 18.110 (6) Å, β = 99.85 (2)°, V = 2258 (1) Å^3, and Z = 4. Diffraction data were collected with a Syntex P2$_1$ automated four-circle diffractometer, and the structure was refined to R_F = 5.4% and R_{wF} = 4.4% for those 2636 reflections with $F_o > \sigma(F_o)$ and $2\theta < 45°$ [Mo Kα radiation]. The molecule consists of a triangular cluster of osmium atoms two of which [Os(1) and Os(3)] are each associated with three terminal carbonyl ligands, while the third [Os(2)] is associated with four. In addition atoms Os(1) and Os(3) are mutually bridged by a hydride ligand (which was located and refined during the course of the analysis) and by a >N=N(p-tol) (p-tol = p-tolyl) ligand. The nonbridged osmium–osmium bond lengths are Os(1)–Os(3) = 2.834 (1) Å and Os(2)–Os(3) = 2.855 (1) Å, while the dibridged Os(2)–Os(3) distance is reduced to 2.823 (1) Å. The osmium–(μ-hydride) distances are equivalent with Os(1)–H = 1.97 (12) Å and Os(3)–H = 2.01 (12) Å. The N(1)–N(2) linkage in the >N=N(p-tol) ligand is 1.238 (18) Å in length—consistent with retention of a formal double bond.

Introduction

For some time we have been interested in the structural chemistry of polynuclear osmium carbonyl hydrides. A particular point of interest has been the geometry of the Os(μ-H)(μ-X)Os bridge in molecules of stoichiometry $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}L)$.[2-7] [Our nomenclature is that X is the bridgehead atom of the uninegatively charged bridging ligand L.] Such molecules have the general core structure I.



I

Table I. Experimental Data for the X-ray Diffraction Study of $(\mu\text{-}H)Os_3(CO)_{10}[\mu\text{-}N{=}N(p\text{-tol})]$

(A) Crystal Parameters[a] at 24 °C

crystal system: monoclinic	a = 9.401 (2) Å
space group: $P2_1/n$[b]	b = 13.463 (4) Å
mol wt = 970.6	c = 18.110 (6) Å
ρ(calcd) = 2.86 g/cm^3	β = 99.85 (2)°
Z = 4	V = 2258 (1) Å^3

(B) Intensity Data

radiation: Mo Kα [$\bar{\lambda}$ = 0.710 730 Å]
monochromator: highly oriented graphite
reflctns measd: $+h,+k,\pm l$
2θ range: 3.5–45.0°
scan type: θ(crystal)–2θ(counter)
scan speed: 2.0°/min
scan range: $[2\theta(K\alpha_1) - 0.9]° \rightarrow [2\theta(K\alpha_2) + 0.9]°$
bkgd measmnt: at beginning and end of scan; each for $^1/_3$ of the total scan time
stds: $4\bar{2}2$, 006, and 263 measured every 47 reflections; no significant deviations
reflctns colltd: 3189 total, yielding 2976 independent
abs coeff: 179.0 cm^{-1}

[a] Based on a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ peaks of 15 reflections with 2θ = 20–30°. [b] Nonstandard setting of the space group $P2_1/c$ [C_{2h}^5, No. 14] having the equipoints $\pm(x, y, z)$ and $\pm(^1/_2 + x, ^1/_2 - y, ^1/_2 + z)$.

We have previously examined the species $(\mu\text{-}H)Os_3(CO)_{10}[\mu\text{-}NHSO_2(p\text{-tol})]$, which has a saturated (4-coordinate) nitrogen present in the Os(μ-H)(μ-N)Os core,[7] and now

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(1) Part 16, $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}OMe)$: Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1980**, *19*, 2391–2395.

(2) Part 2, $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}CHCH_2PMe_2Ph)$: Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 1141–1146.

(3) Part 5, $(\mu\text{-}H)_2Os_3(CO)_{10}$: Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2697–2700.

(4) Part 11, $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}CHCH{=}NEt_2)$: Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1979**, *18*, 848–853.

(5) Part 12, $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}Cl)$: Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1979**, *18*, 1926–1930.

(6) Part 13, $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}Br)$: Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1979**, *18*, 3261–3267.

(7) Part 15, $(\mu\text{-}H)Os_3(CO)_{10}[\mu\text{-}NHSO_2(p\text{-tol})]$: Churchill, M. R.; Hollander, F. J.; Shapley, J. R.; Keister, J. B. *Inorg. Chem.* **1980**, *19*, 1272–1277.

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