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Structure and Bonding in Octafluoro-*trans*-but-2-enebis(triphenylphosphine)platinum, $Pt[CF_3CFCFCF_3][P(C_6H_5)_3]_2$, a Compound with Unusually Long Carbon–Fluorine Bonds

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Abstract: The crystal and molecular structure of a substituted olefin complex of platinum, $Pt[CF_3CFCFCF_3][P(C_6H_5)_3]_2$, has been determined from three-dimensional X-ray diffraction data. The complex crystallizes in space group $P2_1/c$ of the monoclinic system, with four molecules in a unit cell of dimensions $a = 11.635$ (2) Å, $b = 19.213$ (4) Å, $c = 18.107$ (3) Å, $\beta = 114.39$ (2)°. The structural parameters were refined by least-squares techniques, the R factor on F converging to 5.4% for the 3841 independent reflections (measured using a four-circle diffractometer) for which $F^2 > \sigma(F^2)$ and $2\theta \leq 50°$. No symmetry is crystallographically imposed upon the molecules but they have C_2 symmetry to a good approximation. Coordination around platinum is not exactly planar, the largest distortion being the displacement of one olefinic carbon atom by 0.29 (1) Å from the plane defined by the other four atoms; the dihedral angle between the PtP_2 and PtC_2 planes is 10.8 (7)°. The olefinic carbon-carbon separation is 1.429 (14) Å; this value does not differ significantly from the corresponding parameter in the analogous 4,4′-dinitro-*trans*-stilbene complex, suggesting that the separation of the olefinic carbon atoms in complexes of this type formed by acyclic olefins is not a function of the olefinic substituents. The olefinic carbon atoms are essentially equidistant from platinum, the Pt–C distances being 2.028 (12) and 2.048 (11) Å. The Pt–P bond lengths are 2.302 (3) and 2.322 (3) Å. The bonds from each olefinic carbon atom to its fluoro substituent are unusually long at 1.426 (13) and 1.437 (12) Å. The chemical shift in the ^{19}F NMR spectrum of these two fluorine nuclei is much further upfield in the complex than in the free olefin; the chemical shift of the CF_3 resonances does not change greatly upon formation of the complex, and these groups are of normal geometry in the complex. The binding energy of the Pt $4f_{7/2}$ electrons in $Pt[CF_3CFCFCF_3][P(C_6H_5)_3]_2$ is 1.0 eV higher than in the analogous 4,4′-dinitro-*trans*-stilbene complex and is close to that in $PtCl_2[P(C_6H_5)_3]_2$. These results were interpreted to mean that considerable electron density is transferred from platinum to the olefinic fluoro substituents upon formation of the complex. Since the general characteristics of fluoro substituents are such that this electron transfer would be through molecular orbitals of A symmetry, then the Dewar-Chatt-Duncanson model for the bonding in olefin-metal complexes is inappropriate.

Olefins interact to varying degrees with transition metal compounds, in some cases forming isolable complexes in which the structure and properties of the olefin moiety are modified, with the result that the reactivity of the olefin toward additional reagents is also modified. In order to design transition metal compounds that might confer unusual reactivity upon olefins, it is necessary to determine the changes in olefin geometry that occur upon interaction with a metal. The class of compounds of general formula $Pt[L][P(C_6H_5)_3]_2$, where L is an olefin, is suitable for a systematic study of the geometry of olefins in stable complexes because a wide range of olefins form such complexes[2,3] and also because steric constraints are not imposed upon the olefin by the rest of the molecule. In the first paper[4] of a series from this laboratory in which the structure and properties of selected olefin-bis(triphenylphosphine)platinum complexes are to be reported, the olefin was 4,4′-dinitro-*trans*-stilbene, chosen because it forms a very stable complex[2a] and because the substituents upon the olefin are powerfully electron withdrawing in a π-fashion. In the complex, the olefin substituents manifestly utilize their electron-withdrawing ability to the maximum extent possible, since the planes of the 4-nitrophenyl substituents are perpendicular to the plane defined by the platinum and olefinic carbon atoms, in spite of the fact that this orientation is relatively unfavorable in terms of intraolefin contacts. The separation of the olefin carbon atoms was 1.42 (2) Å in this complex, which is among the shortest observed in this type of compound. Several other complexes of this general formula have been the subject of X-ray diffraction experiments,[5-10] but relatively few of the reported structures are of high precision; the present studies were undertaken to define more clearly the relationships between the steric and electronic effects of the olefin substituents and the structure adopted by the olefin upon coordination.

The most obvious choice of an olefin with characteristics totally different from 4,4′-dinitro-*trans*-stilbene is tetrafluoroethylene, since the fluoro substituents are electron withdrawing in a σ-fashion and electron donating in a π-fashion.[11] However, there have been problems of crystallographic disorder in at least one complex of tetrafluoroethylene[12] and in $Pt[CF_2CFCl][P(C_6H_5)_3]_2$ and $Pt[CF_2CCl_2][P(C_6H_5)_3]_2$;[7] consequently, tetrafluoroethylene was not chosen for this study. This paper presents the results of an X-ray diffraction study on the complex formed by octafluoro-*trans*-but-2-ene, chosen because the olefin has characteristics similar in an overall sense to tetrafluoroethylene and because the complex seemed unlikely to have disorder problems since the relatively large trifluoromethyl substituents should have specific steric requirements.

The olefin-metal bonding interaction can be considered to have two components: a redistribution of the bonding electrons of the olefin through the intermediacy of the metal or a net transfer of electrons from the metal to the olefin. In a formal sense, the first corresponds to attainment of an excited state electronic configuration[13] for the olefin and the second to reduction of the olefin. This second factor would give rise to a positive charge upon the metal and thus its importance can, in principle, be determined using the ESCA technique. Previously reported ESCA results are contradictory. Two papers[14,15] suggest that the binding energy of the platinum $4f_{7/2}$ electrons in a number of compounds related to the title compound is quite sensitive to the nature of the ligands around platinum, whereas other papers[16,17] indicate the opposite situation to be correct. Results reported here for three compounds support the former view and this will be shown to be consistent with structural and ^{19}F NMR results.

Experimental Section

(i) **Synthesis and ^{19}F NMR spectrum of Octafluoro-*trans*-but-2-enebis(triphenylphosphine)platinum, $Pt[CF_3CFCFCF_3][P(C_6H_5)_3]_2$.** All reactions were performed under a nitrogen atmosphere using Schlenk apparatus. The procedure is related to that already reported.[3] Tetrakis(triphenylphosphine)platinum, $Pt[P(C_6H_5)_3]_4$, was prepared by a literature method.[18] An excess of octafluoro-*trans*-but-2-ene, C_4F_8, was passed into a solution of $Pt[P(C_6H_5)_3]_4$, 1.0 g, in benzene, 25 ml, at room temperature. The mixture was refluxed for 5 hr using a solid CO_2–acetone condenser and then 10 ml of solvent was distilled off. The clear solution was cooled to room temperature, whereupon crystals, 0.6 g (80%), of $Pt[CF_3CFCFCF_3][P(C_6H_5)_3]_2$ separated. The desired product was recrystallized from a methanol–methylene chloride mixture to obtain crystals suitable for an X-ray diffraction experiment. Anal. Calcd for $PtP_2F_8C_{40}H_{30}$: P, 6.7; C, 52.2; H, 3.3. Found: P, 6.7; C, 52.4; H, 3.2.

The ^{19}F NMR spectrum was measured on an HA100 modified to run at 94.0 MHz with benzotrifluoride as an internal reference. The observed CF_3 resonances (essentially a doublet but with a fraction of this intensity split further by ^{195}Pt) are as reported,[3a] free rotation about the olefin–platinum axis not occurring at room temperature. The structure of the high field line, assigned to the CF resonances, was resolved into a triplet (with a fraction split further by ^{195}Pt), suggesting the two phosphorus nuclei accidentally couple equally: $J_{P-F} = 26.6$, $J_{Pt-F} = 67.6$ Hz. We thank J. W. Faller for running this spectrum.

(ii) **ESCA Data.** The spectra were recorded on a Hewlett-Packard 5950 A instrument using monochromatized Al Kα X-radiation and an electron flood gun operating at 0.6 mA to minimize charging effects. The samples were prepared on gold-plated sample holders each in three different ways, evaporation of a methylene chloride solution, direct pressing, and in a graphite pellet. The following binding energies were calculated (in eV) using a standard value of 285.0 eV for the carbon 1s binding energy: $PtCl_2[P(C_6H_5)_3]_2$, Pt $4f_{7/2}$ 73.3, P 2p 132.3; $Pt[CF_3CFCFCF_3][P(C_6H_5)_3]_2$, Pt $4f_{7/2}$ 73.0, P 2p 132.3, F $1s_{1/2}$ 688.3; $Pt[(C_6H_4NO_2)CHCH(C_6H_4NO_2)][P(C_6H_5)_3]_2$, Pt $4f_{7/2}$ 72.0, P 2p 132.3. The reproducibility of these data was good and the standard deviation of any of these binding energies was <0.2 eV.

Collection and Reduction of X-Ray Diffraction Data. The crystal was assigned to the monoclinic system on the basis of optical examination and preliminary X-ray photography. The observed systematic absences are $h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$, which is consistent with the space group $C_{2h}{}^5$, $P2_1/c$. The cell constants, obtained by least-squares refinement using the setting angles of 12 reflections centered on a Picker four-circle automatic diffractometer with Mo $K\alpha_1$ X-radiation (λ 0.70930 Å) are (at 20°): $a = 11.635$ (2), $b = 19.213$ (4), $c = 18.107$ (3) Å; $\beta = 114.39$ (2)°. For four formula weights of the molecule in the unit cell, the calculated density is 1.66 g/cm^3; the observed density (by flotation) is 1.63 g/cm^3. No symmetry is crystallographically imposed upon the molecules.

The crystal used in data collection was bounded by the faces {010}, {011} and $\{11\bar{1}\}$, the lengths of the normals from the faces to the center of the crystal were 0.045, 0.075 and 0.175 mm for the sets, respectively. The crystal was initially aligned about the *a* axis of the cell and was misset before data collection. The intensity data were collected by using a Picker four-circle automatic diffractometer in ω–2θ scan mode with crystal monochromated Mo Kα X-radiation. A symmetric scan of 1.4° in 2θ was used with a scan rate of 2°/min. Stationary-crystal, stationary-counter background counts of 4 sec were measured at each end of the scan. The intensities of the symmetry equivalent reflections $hkl^{\pm}$ and $h\bar{k}l^{\pm}$ were recorded out to a 2θ value of 50°. The intensities of three standard reflections were measured at intervals throughout data collection; these intensities did not vary by more than ±2% during the experiment and thus crystal decomposition was negligible.

The data were corrected for background and the changes in the standard reflections. The linear absorption coefficient is 37.3 cm^{-1}, and corrections were applied,[19] the transmission coefficients ranging between 0.55 and 0.76. Equivalent reflections were averaged and the *R* factor of averaging ($R_{av} = 100(I_1 - I_2)/(I_1 + I_2)$, where I_1 and I_2 are the two corrected intensities) was 2.2% for those 1056 reflections classed as observed and measured more than once. The independent reflections were corrected for Lorentz-polarization effects. Individual standard deviations, $\sigma(F^2)$, of the corrected intensities were calculated from counting statistics and from the range of symmetry-equivalent reflections, the larger estimate being assigned to the reflection. A total of 12,843 reflections were measured and processed. There were 6496 independent reflections, of which 3841 had a net intensity greater than $\sigma(F^2)$ for that reflection. There were 1246 independent reflections that could be classed as observed using the criterion that at least one of the measured net intensities be greater than three times the estimated standard deviation, calculated from counting statistics, of the background counts.

Solution and Refinement of the Structure. Initial values for the fractional coordinates of the platinum and phosphorus atoms were obtained from a three-dimensional Patterson function.[19] Succeeding applications of least-squares refinement and difference Fourier calculations yielded the coordinates of all non-hydrogen atoms, the carbon atoms of the phenyl rings being refined as groups. The scattering factors were calculated using analytical approximations for neutral atoms[20] and the effects of anomalous dispersion[21] were included in F_c. The function minimized in refinement was $\Sigma w||F_o| - |F_c||^2$, where $w = 4F_o{}^2/\sigma^2(F_o{}^2)$. Isotropic thermal parameters were used for all atoms, with only one overall thermal parameter for each group, and the *R* factor (on F) converged to 4.0% for the 1246 reflections classed as observed. The platinum, phosphorus, and fluorine atoms were then refined with anisotropic thermal parameters, individual thermal parameters were refined for the carbon atoms in the groups, and the scattering of the hydrogen atoms of the phenyl groups was included, assuming an idealized group geometry with a C–H bond length of 0.95 Å and thermal parameters 0.3 Å^2 higher than the carbon atoms to which they are bound; the *R* factor decreased to 2.1% after two cycles of refinement. There was a systematic variation of the individual thermal parameters of the group atoms and an overall thermal parameter was defined (and subsequently refined) for each group, and the differences (not subsequently varied) from this overall parameter for each of the positions around the ring were averaged for all of the

Table I. Positional and Thermal Parameters for the Nongroup Atoms in $Pt[CF_3CFCFCF_3][P(C_6H_5)_3]_2$

Atom	x	y	z	B_{iso} (Å^2) or β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	0.23299 (4)	0.01047 (2)	−0.21947 (3)	0.00665 (4)	0.00174 (1)	0.00291 (2)	−0.00028 (3)	0.00228 (2)	0.00004 (2)
P(1)	0.1286 (2)	−0.0084 (2)	−0.1362 (2)	0.0066 (3)	0.0019 (1)	0.0031 (1)	0.0001 (2)	0.0022 (2)	0.0004 (1)
P(2)	0.2300 (3)	−0.0945 (2)	−0.2186 (2)	0.0099 (5)	0.0024 (1)	0.0037 (2)	−0.0009 (2)	0.0035 (3)	−0.0005 (1)
F(1)	0.4297 (7)	0.0805 (3)	−0.2595 (5)	0.0158 (12)	0.0043 (3)	0.0079 (5)	−0.0007 (5)	0.0064 (7)	0.0005 (3)
F(2)	0.1829 (7)	0.1652 (4)	−0.2346 (5)	0.0149 (12)	0.0039 (3)	0.0083 (5)	0.0005 (4)	0.0054 (7)	0.0006 (3)
F(3)	0.2630 (10)	0.0700 (4)	−0.4086 (5)	0.0421 (22)	0.0058 (4)	0.0054 (5)	0.0040 (7)	0.0104 (9)	0.0016 (3)
F(4)	0.2527 (8)	0.1728 (4)	−0.3702 (5)	0.0224 (14)	0.0035 (3)	0.0073 (5)	0.0000 (5)	0.0060 (7)	0.0025 (3)
F(5)	0.1085 (8)	0.0991 (4)	−0.3817 (5)	0.0153 (13)	0.0064 (4)	0.0048 (4)	−0.0019 (5)	0.0000 (6)	0.0025 (3)
F(6)	0.4746 (6)	0.1019 (3)	−0.1007 (4)	0.0093 (9)	0.0042 (3)	0.0055 (4)	0.0003 (4)	0.0012 (5)	−0.0000 (3)
F(7)	0.4319 (7)	0.2028 (3)	−0.1577 (4)	0.0193 (12)	0.0035 (3)	0.0065 (5)	−0.0047 (5)	0.0051 (6)	−0.0007 (3)
F(8)	0.3417 (7)	0.1691 (3)	−0.0820 (4)	0.0178 (12)	0.0038 (3)	0.0050 (4)	−0.0023 (4)	0.0056 (6)	−0.0011 (3)
C(1)	0.3001 (12)	0.0829 (6)	−0.2731 (8)	4.0 (3)					
C(2)	0.2811 (11)	0.1137 (6)	−0.2071 (7)	3.4 (3)					
C(3)	0.2327 (16)	0.1060 (8)	−0.3584 (10)	6.0 (4)					
C(4)	0.3814 (14)	0.1465 (7)	−0.1372 (8)	4.5 (3)					

[a] The form of the anisotropic thermal ellipsoid is $\exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\}$

Table II. Group[a] Parameters[b] in $Pt[CF_3CFCFCF_3][P(C_6H_5)_3]_2$

Group	x_c	y_c	z_c	δ	ϵ	η
1A	0.2751 (5)	0.0767 (2)	0.0288 (3)	0.979 (5)	−2.938 (4)	0.780 (4)
1B	0.0826 (5)	−0.1625 (3)	−0.0804 (3)	−1.252 (8)	−2.244 (5)	0.583 (8)
1C	−0.1518 (5)	0.0550 (2)	−0.2174 (3)	2.702 (8)	−2.296 (5)	−0.058 (7)
2A	0.3398 (6)	−0.0818 (3)	−0.4179 (4)	1.803 (6)	2.755 (8)	−1.581 (5)
2B	0.3957 (4)	−0.2192 (2)	−0.1696 (3)	−2.613 (12)	1.986 (5)	1.669 (12)
2C	−0.0519 (6)	−0.1542 (3)	−0.3724 (3)	−2.799 (6)	−3.100 (5)	−0.066 (5)

[a] The groups are all phenyl rings, and each set of six parameters applys to the carbon and to the hydrogen atoms of that ring. [b] The parameters have been defined previously: R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4,** 773 (1965).

rings.[4] The mean differences are the following: C(1), −1.65; C(2) and C(6), −0.05; C(3) and C(5), 1.15; C(4), 1.25 Å^2. Two cycles of refinement were performed using all 3841 reflections with $F^2 > \sigma(F^2)$ and, in the final cycle, no parameter changed by more than one-tenth of its esd. The final values of the R factor and weighted R factor

$$R_w = (\Sigma w(F_o - F_c)^2/wF_o^2)^{1/2}$$

were 5.4 and 4.0%. The error in an observation of unit weight was 0.68, less than unity, probably due to a small overweighting of the stronger reflections. A final difference Fourier showed no peaks higher than 0.2 Å^{-3}.

The final values of the positional and thermal parameters for the nongroup atoms and their standard deviations calculated from the inverse matrix are given in Table I.[22] The phenyl ring atoms were refined as groups and the parameters are given in Table II. Table III lists the fractional coordinates (derived from the group parameters) and the thermal parameters for the carbon atoms in the groups. Table IV gives the root-mean-square amplitudes of vibration for those atoms refined with anisotropic thermal parameters; for the fluorine atoms the angles made by the principal axes of vibration to the C-F bond vectors are given.

Description of the Structure

The crystal structure consists of the packing of the monomeric molecular units $Pt[CF_3CFCFCF_3][P(C_6H_5)_3]_2$; there are no exceptionally short intermolecular contacts. The separation of the olefinic carbon atoms C(1) and C(2) is 1.429 (14) Å, which is not significantly different from 1.416 (15) Å, the corresponding distance observed in $Pt[(C_6H_4NO_2)CHCH(C_6H_4NO_2)][P(C_6H_5)_3]_2$.[4] The C(1)-Pt-C(2) angle is 41.0 (4)° and the P(1)-Pt-P(2) angle is 105.9 (1)°, neither being unusual. An overall view of the molecule is given in Figure 1. Coordination around platinum is only approximately planar, the dihedral angle between the Pt, C(1), C(2) and the Pt, P(1), P(2) planes (the PtC_2 and PtP_2 planes) being 10.8 (7)°; C(1) and C(2) are displaced by 0.29 (1) and 0.06 (1) Å from the PtP_2 plane.

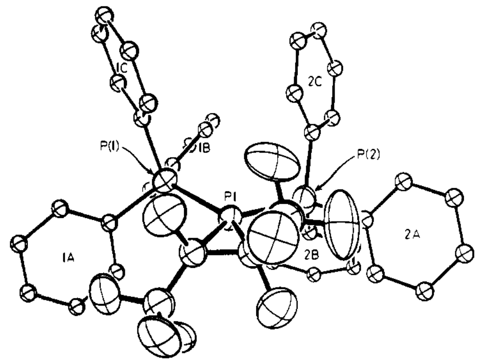

Figure 1. General view of a molecule of $Pt[CF_3CFCFCF_3][P(C_6H_5)_3]_2$. The atoms are represented by 50% probability ellipsoids, except the carbon atoms of the triphenylphosphine ligands which have been assigned artificially low thermal parameters for the purpose of clarity. The hydrogen atoms of the triphenylphosphine ligands are omitted. The ring nomenclature is specified in this figure.

Figure 2 shows the coordination sphere around platinum and details of the coordinated olefin moiety from a viewpoint normal to the PtC_2 plane and above the centroid of the Pt, C(1), C(2) triangle. The two substituent planes F(1), C(1), C(3) and F(2), C(2), C(4) are almost exactly perpendicular to the PtC_2 plane, the dihedral angles being 93.0 (6) and 93.2 (6)°, respectively. The deviations from perpendicularity are in the sense that displaces F(1) toward C(4) and F(2) toward C(3) and no particular significance is attached to the deviations. The dihedral angle between the two substituent planes is 80 (1)° and each substituent plane is bent back by 40 (1)° away from the metal. The olefin-metal fragment of the complex molecule has symmetry which closely approximates C_2 and Table V lists pairs of parameters related by the (approximate) twofold axis. With the exception of the Pt-P bond lengths, none of the parameters listed in the first column of Table V differs significantly

Table III. Thermal Parameters and Derived Fractional Coordinates[a] of Phenyl Group Carbon Atoms in $Pt[CF_3CFCFCF_3][P(C_6H_5)_3]_2$

Ring	Atom	B_{iso} (Å^2)	x	y	z
1A	C(1)	1.9	0.2071	0.0395	−0.0425
	C(2)	3.5	0.1501	0.0921	−0.0175
	C(3)	4.7	0.2179	0.1288	0.0532
	C(4)	4.8	0.3422	0.1134	0.0991
	C(5)	4.7	0.3997	0.0614	0.0751
	C(6)	3.5	0.3327	0.0244	0.0044
1B	C(1)	2.5	0.1021	−0.0949	−0.1018
	C(2)	4.1	0.1588	−0.1169	−0.0220
	C(3)	5.3	0.1392	−0.1840	−0.0011
	C(4)	5.4	0.0634	−0.2292	−0.0594
	C(5)	5.3	0.0068	−0.2081	−0.1386
	C(6)	4.1	0.0258	−0.1411	−0.1600
1C	C(1)	3.0	−0.0300	0.0269	−0.1821
	C(2)	4.6	−0.1231	0.0039	−0.1592
	C(3)	5.8	−0.2437	0.0320	−0.1943
	C(4)	5.9	−0.2719	0.0828	−0.2522
	C(5)	5.8	−0.1806	0.1060	−0.2407
	C(6)	4.6	−0.0597	0.0783	−0.2407
2A	C(1)	5.7	0.2909	−0.0875	−0.3592
	C(2)	7.3	0.2143	−0.0978	−0.4405
	C(3)	8.5	0.2632	−0.0922	−0.4984
	C(4)	8.6	0.3879	−0.0763	−0.4757
	C(5)	8.5	0.4648	−0.0659	−0.3955
	C(6)	7.3	0.4168	−0.0714	−0.3371
2B	C(1)	2.7	0.3238	−0.1654	−0.2198
	C(2)	4.3	0.3829	−0.2141	−0.2486
	C(3)	5.5	0.4541	−0.2672	−0.1987
	C(4)	5.6	0.4666	−0.2721	−0.1202
	C(5)	5.5	0.4086	−0.2243	−0.0910
	C(6)	4.3	0.3372	−0.1710	−0.1404
2C	C(1)	3.7	0.0722	−0.1296	−0.3344
	C(2)	5.3	0.0474	−0.2003	−0.3408
	C(3)	6.5	−0.0758	−0.2245	−0.3786
	C(4)	6.6	−0.1742	−0.1785	−0.4099
	C(5)	6.5	−0.1509	−0.1084	−0.4040
	C(6)	5.3	−0.0281	−0.0837	−0.3663

[a] The estimated standard deviations obtained from the inverse matrix for these parameters average 0.2, 0.0009, 0.0005, and 0.0005, respectively. This estimate is too low because errors in the model (which describes these atoms as groups) are not included.

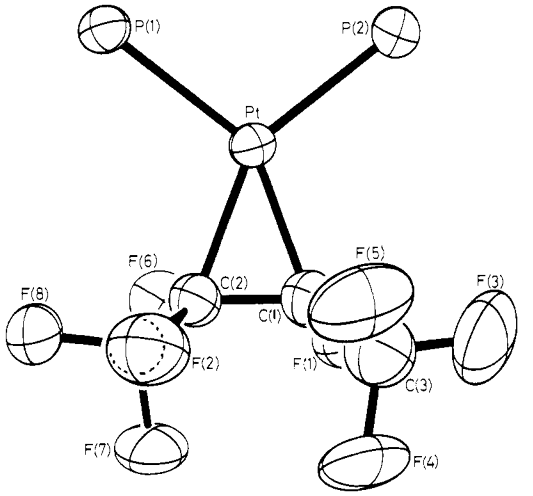

Figure 2. $Pt[CF_3CFCFCF_3][P(C_6H_5)_3]_2$ from a viewpoint normal to the PtC_2 plane and above the centroid of the Pt, C(1), C(2) triangle. The carbon and hydrogen atoms of the triphenylphosphine ligands have been omitted. The other atoms are represented by 50% probability ellipsoids. The atom C(4) is obscured by F(2) and is indicated by non-continuous outlines; this is not done for other obscurations. The atom nomenclature is specified in this figure.

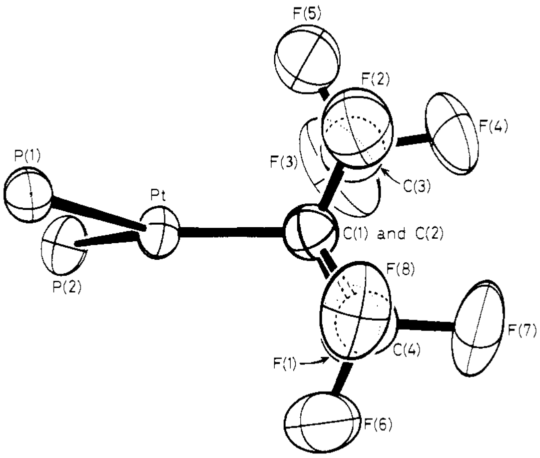

Figure 3. $Pt[CF_3CFCFCF_3][P(C_6H_5)_3]_2$ viewed along the C(2), C(1) vector and including the same atoms as in Figure 2.

from the corresponding parameter in the second column. Figure 3 shows the molecule viewed along the C(2), C(1) vector and this further emphasizes how close to having C_2 symmetry is the olefin-metal fragment.

The directions of the principal axes of vibration of the platinum and two phosphorus atoms are indicated in Figures 1-3. None of these atoms vibrates with great anisotropy, and the Pt-P bond lengths corrected for thermal motion using the riding model are 2.323 (3) and 2.309 (3) Å. The difference between the two Pt-P bond lengths, 0.014 (4) Å, is just statistically significant but cannot be ascribed to an effect transmitted from the olefin-metal interaction (since this latter is symmetrical). Phenyl ring 1B is unusual: the angle Pt-P(1)-1BC(1) is 125 (1)°, significantly larger than any of the other five Pt-P-C angles, which average 113°. There is also a difference (not of high statistical significance) in the P-C bond lengths, P(1)-1BC(1) being 1.85 Å and the other five averaging 1.81 Å. The difference between the Pt-P bond lengths may be linked with the distortion of the phenyl ring array around P(1).

Particularly remarkable are the lengths of the C(1)-F(1)

Table IV. Root-Mean-Square Amplitudes (Å) and Directions[a] of Principal Axes of Vibration for $Pt[CF_3CFCFCF_3][P(C_6H_5)_3]_2$

Atom	Axis of min vibration		Axis of intermediate vibration		Axis of max vibration	
Pt	0.170 (1)		0.189 (1)		0.205 (1)	
P(1)	0.177 (6)		0.190 (5)		0.216 (5)	
P(2)	0.196 (6)		0.199 (5)		0.256 (5)	
F(1)	0.25 (1)	[48 (8)]	0.30 (1)	[55 (10]	0.34 (1)	[65 (10)]
F(2)	0.27 (1)	[77 (17)]	0.28 (1)	[116 (12)]	0.34 (1)	[29 (7)]
F(3)	0.21 (1)	[162 (5)]	0.32 (1)	[75 (5)]	0.50 (1)	[100 (2)]
F(4)	0.18 (1)	[14 (3)]	0.36 (1)	[87 (8)]	0.36 (1)	[103 (19)]
F(5)	0.21 (1)	[147 (7)]	0.28 (1)	[59 (7)]	0.42 (1)	[81 (3)]
F(6)	0.22 (1)	[10 (6)]	0.28 (1)	[91 (9)]	0.31 (1)	[80 (6)]
F(7)	0.18 (1)	[17 (4)]	0.29 (1)	[104 (4)]	0.38 (1)	[99 (3)]
F(8)	0.23 (1)	[14 (21)]	0.24 (1)	[100 (29)]	0.34 (1)	[100 (4)]

[a] The directions are indicated for the fluorine atoms only and are with respect to the appropriate C−F bond axis.

Table V. Molecular Parameters[a] in $\mathrm{Pt[CF_3CFCFCF_3][P(C_6H_5)_3]_2}$

Parameter 1		Parameter 2	
	(a) Bond Lengths (Å)		
Pt-P(1)	2.322 (3)	Pt-P(2)	2.302 (3)
Pt-C(2)	2.048 (11)	Pt-C(1)	2.028 (12)
C(2)-F(2)	1.437 (12)	C(1)-F(1)	1.426 (13)
C(2)-C(4)	1.464 (15)	C(1)-C(3)	1.483 (17)
C(4)-F(6)	1.326 (13)	C(3)-F(5)	1.334 (15)
C(4)-F(7)	1.352 (13)	C(3)-F(4)	1.336 (15)
C(4)-F(8)	1.335 (13)	C(3)-F(3)	1.301 (15)
	(b) Bond Angles (deg)		
P(1)-Pt-C(2)	105.9 (3)	P(2)-Pt-C(1)	107.3 (4)
Pt-C(2)-C(1)	68.7 (7)	Pt-C(1)-C(2)	70.2 (7)
Pt-C(2)-F(2)	119.2 (7)	Pt-C(1)-F(1)	118.9 (8)
Pt-C(2)-C(4)	127 (1)	Pt-C(1)-C(3)	124 (1)
C(1)-C(2)-F(2)	112 (1)	C(2)-C(1)-F(1)	113 (1)
C(1)-C(2)-C(4)	124 (1)	C(2)-C(1)-C(3)	123 (1)
F(2)-C(2)-C(3)	104 (1)	F(1)-C(1)-C(3)	105 (1)
	(c) Torsion Angles (deg)		
Pt-C(1)-C(2)-F(2)	114.1 (8)	Pt-C(2)-C(1)-F(1)	114.0 (9)
Pt-C(1)-C(2)-C(4)	121 (1)	Pt-C(2)-C(1)-C(3)	119 (1)
F(1)-C(1)-C(2)-C(4)	7 (2)	F(2)-C(2)-C(1)-C(3)	5 (2)

[a] The olefin-metal fragment of the complex molecular has symmetry which closely approximates C_2, the axis passing through Pt and the mid-point of the C(1), C(2) bond vector. Parameters 1 and 2 are interchanged by operation of this symmetry element.

and C(2)-F(2) bonds, which average 1.43 Å. Both of these bonds are significantly longer than any previously reported carbon-fluorine bond, for which typical lengths are in the range 1.30-1.38 Å.[11,23] The CF_3 groups are of normal geometry: the six C-F bonds average 1.33 Å in length, the F-C-F angles range from 106 (1) to 108 (1)°, average 107°, and the C-C-F angles range from 110 (1) to 114 (1)°, average 112°. The shortest nonbonded F-F contacts are within the CF_3 groups, these ranging from 2.11 (1) to 2.16 (1) Å, average 2.14 Å. The nearest fluorine approaches to F(1) are F(3) 2.60 (1), F(4) 2.83 (1), F(6) 2.73 (1), and F(7) 2.98 (1) Å; analogous approaches to F(2) are F(8) 2.61 (1), F(7) 2.74 (1), F(5) 2.75 (1), and F(4) 2.89 (1) Å. The vibrations of the fluorine atoms seem reasonable, those of F(1) and F(2) not being very anisotropic and those of the fluorine atoms of the CF_3 groups having the axes of minimum and maximum vibration approximately parallel and normal, respectively, to the appropriate C-F bond axis (see Table IV).

Bonding in $\mathrm{Pt[CF_3CFCFCF_3][P(C_6H_5)_3]_2}$. The most remarkable feature of this molecule is the length of the bonds between each olefinic carbon atom and its fluoro substituent, the average of the two independent lengths being 1.43 Å. This and other properties (specifically the ^{19}F NMR and ESCA spectra) of the molecule indicate that a considerable negative charge can be associated with the fluoro substituents, a relatively ionic fluorine naturally yielding a long C-F bond length. From the general characteristics of a fluoro substituent, it can be assumed that this electron density is removed from the *A* symmetry molecular orbitals and this should affect the whole molecule. A comparison of the structure of the title compound with that reported[24] for $\mathrm{Pt[CF_3CCCF_3][P(C_6H_5)_3]_2}$ reveals trends expected on this basis. In the acetylene complex both the Pt-C and Pt-P separations are shorter than in the olefin complex, in spite of the fact that there is considerable positive charge (as indicated by the ESCA spectrum) associated with the platinum atom in the olefin complex; the ESCA spectrum of the acetylene complex has not been examined but the binding energy of its Pt $4f_{7/2}$ electrons is unlikely to be greater than in the olefin complex.

The normal range of C-F bond lengths in a wide variety of compounds is 1.30-1.38 Å.[11,23] In the archetype of uncoordinated fluoroolefins, tetrafluoroethylene, the C-F bond length is 1.31 (1) Å[25] and this increases to about 1.35 Å upon coordination to a metal.[26] However, the structure of octafluoro-*trans*-but-2-ene has not been determined and there is considerable controversy about the structure of the most closely related olefin that has been examined, hexafluoropropene.[27] Thus it is not clear what the olefinic carbon to fluorine bond length in octafluoro-*trans*-but-2-ene is, but the ^{19}F NMR spectrum shows that a large change in the environment of those two fluorine nuclei occurs upon formation of the complex with platinum, the chemical shift of the resonances being 136.5 ppm further upfield in the complex than in the free olefin.[3a] No large change occurs in the chemical shift of the CF_3 resonances upon coordination and the geometry of these groups in the complex is normal. The binding energy of the F $1s_{1/2}$ electrons was not sensitive to the difference between the chemical types of fluorine atom, only one peak of half-height width about 3 eV being observed in the ESCA spectrum.

The ESCA results reported in this paper indicate a significant difference between the binding energy of the Pt $4f_{7/2}$ electrons in the complexes formed by octafluoro-*trans*-but-2-ene and 4,4′-dinitro-*trans*-stilbene: in the former complex the binding energy is almost as high as in the divalent platinum compound $\mathrm{PtCl_2[P(C_6H_5)_3]_2}$, whereas in the latter complex the binding energy is significantly lower and close to that in the zerovalent platinum compound $\mathrm{Pt[P(C_6H_5)_3]_4}$.[14,15] The total olefin-metal interaction in any complex is a composite of a redistribution of the bonding electrons of the olefin through the intermediacy of the metal and a transfer of electrons from the metal to the olefin and there is a distinct difference between the relative contributions of these two components to the bonding in the olefin complexes under discussion. In the nitrostilbene complex, the major component is a redistribution of the bonding electrons of the olefin and the Dewar-Chatt-Duncanson model for the bonding is appropriate. In the fluoroolefin complex, however, this model does not provide a good description of the bonding since the concept of donation of electrons from the olefin π-orbital to the metal (the resultant molecular orbital being of *A* symmetry) is unrealistic since there is a net transfer of electrons from the metal to the olefin via orbitals of *A* symmetry. The three-center molecular orbital scheme proposed previously[4,28] can be used in all olefin complexes by considering how the olefin sub-

Table VI. Structural Parameters for Compounds of General Formula Pt[L] [P(C_6H_5)$_3$]$_2$, where L is an Olefin, R_2CCR_2

L	Separation of olefinic C atoms	Pt–C separations	Pt–P separations	Dihedral angle between CR$_2$ planes	Dihedral angle between PtP$_2$ and PtC$_2$ planes	Ref
($C_6H_4NO_2$)CHCH($C_6H_4NO_2$)	1.42 (2)	2.17 (1) 2.09 (1)	2.261 (4) 2.298 (4)	38	8.7 (7)	4
$Cl_2CC(CN)_2$	1.42 (3)	2.10 (2) 2.00 (2)	2.260 (6) 2.339 (6)	62 (3)	2 (1)	8
$CF_3CFCFCF_3$	1.43 (1)	2.05 (1) 2.03 (1)	2.302 (3) 2.322 (3)	80	10.8 (7)	This paper
H_2CCH_2	1.43 (1)	2.12 (1) 2.11 (1)	2.270 (2) 2.265 (2)	*a*	2	10
$(CN)_2CC(CN)_2$	1.49 (5)	2.12 (3) 2.10 (3)	2.291 (9) 2.288 (8)	64	8	6
(CN)HCCH(CN)	1.53 (4)	2.16 (2) 2.05 (2)	2.296 (4) 2.277 (5)	*a*	5	5
Cl_2CCCl_2	1.62 (3)	2.05 (3) 2.02 (3)	2.278 (8) 2.292 (7)	81 (2)	12 (2)	7

[a] Cannot be determined from the data reported.

stituents (and other changes) affect the polarity of the three occupied orbitals.

An important conclusion to be drawn from this experiment is that the separation of the olefinic carbon atoms in the complex formed by octafluoro-*trans*-but-2-ene is not significantly different from the corresponding separation in the 4,4′-dinitro-*trans*-stilbene complex,[4] despite the large differences between the olefinic substituents. This permits consideration of the following hypothesis; in compounds of general formula Pt[L][P(C_6H_5)$_3$]$_2$, where L is an olefin, the separation of the olefinic carbon atoms remains essentially constant at 1.42 Å for all olefins (except those with significant ring strain). Table VI lists selected parameters of all compounds of this type formed by acyclic olefins whose structures have been reported; the list is ordered in terms of increasing separation of the olefinic carbon atoms. For the first four compounds, the separation of the olefinic carbon atoms is constant within experimental error. It is important to recognize that the other structures were determined to a lower degree of precision and certainly the tetracyanoethylene[5] and dicyanoethylene[6] results do not contradict the hypothesis. The tetrachloroethylene complex, with its very long carbon-carbon separation, apparently contradicts the hypothesis but there are sufficient uncertainties associated with that experiment[7] to require further work before the hypothesis can be rejected.

The platinum–carbon separations are strongly influenced by the nature of the olefinic substituents and there is an inverse relationship between the Pt–C and Pt–P separations (see Table VI). The bonding model already proposed[4] can be used to rationalize these observations, the short Pt–C (and hence long Pt–P) separations in title compound being due to relatively high electron density in the Pt–C regions resulting from the π-donating ability of the fluoro substituents (or, more precisely, the ability of the fluoro substituents to donate electrons into the orbitals of B symmetry in this complex). A further manifestation of the high electron density localized in the Pt–C regions is that the olefin substituents are considerably bent away from the coplanar arrangement they have in the free olefin, as shown in Figure 2.

There is a dihedral angle of 10.8 (7)° between the PtP$_2$ and PtC$_2$ planes in the title compound. Such dihedral angles have been observed in a wide variety of related compounds, but no explanation of this phenomenon has previously been suggested. By analogy with Pt(CO)$_2$[P(C_6H_5)$_3$]$_2$, a biscarbene complex of platinum, Pt(CR_2)$_2$[P(C_6H_5)$_3$]$_2$, can be imagined in which this dihedral angle would be 90°. Other characteristics of this hypothetical molecule would be short Pt–C separations and a large dihedral angle between the CR$_2$ planes. These characteristics are all present to some degree in the title compound, and thus there could be a small contribution of a biscarbene canonical form to the overall bonding in the molecule. Some weight is lent to this tentative suggestion by the structure reported[7] for the tetrachloroethylene complex (although there are the uncertainties mentioned above) since it exhibits all of these characteristics to about the same extent, as examination of Table VI will reveal. This would also explain why, in compounds of this general formula, there is not free rotation about the olefin–metal axis in solution[3] as has been observed for other olefin complexes;[29] if a 90° rotation were achieved, the olefinic carbon–carbon bond order would be reduced to zero, the resultant biscarbene complex would be highly reactive, and a chemical change would likely occur. Stabilization of such a carbene with appropriate substituents is possible,[30] but more interesting are the reactions that may occur at appropriate temperatures.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JACS-75-4232.

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Mechanism of Base Promoted Reduction of Nickel(III) Complexes of Macrocyclic Amines. A Coordinated Ligand Radical Intermediate

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Abstract: The mechanisms of decomposition of two nickel(III) complexes which contain macrocyclic secondary amine ligands have been studied. When **2** is treated with basic solvents such as pyridine, triethylamine, or water a Ni(II) ligand radical species is formed according to: $\mathrm{N^{III}N{\leqq}H + B \rightarrow Ni^{II}N{<}\cdot + BH^{+}}$. Chemical and spectroscopic evidence is presented in support of this species. A similar species is observed in the decomposition of **4** by pyridine but is not observed in water although product analyses suggest that a radical species is again formed. Depending upon the solvent 1–25% of the radicals formed decompose with rupture of the macrocyclic ring; the remainder are converted to Ni(II) tetramine complex by hydrogen abstraction from ligand fragments or from a second radical species. The latter process leads to monoimine complex formation. Under certain conditions monoimine may also be formed by oxidation of the Ni(II) ligand radical by Ni(III) complex. Such radical species have been proposed earlier as intermediates in macrocyclic amine complex reactions, but no direct evidence for their formation has previously been obtained.

Nickel(II) complexes of macrocyclic ligands of the 1,4,8,11-tetraazacyclotetradecane (cyclam) class have received a great deal of attention in the past several years.[1] More recently reports of nickel(III) complexes with these ligands have appeared.[2] The strong ligand field exerted by these macrocyclic ligands on the nickel(II) ion raises antibonding orbital energies sufficiently that removal of an electron is a low energy process. The charge placed on the metal ion by the four planar nitrogen donors stabilizes the resultant trivalent oxidation state. Similar arguments account for the formation and stabilities of Cu(III),[3] Ag(II),[4,5] and Ag(III)[5] complexes of these ligands.

Nickel(III) complexes of these tetramine ligands are easily formed by electrochemical and chemical oxidation and most of these are stable to reduction indefinitely as solids in a dry atmosphere and for extended periods in purified acetonitrile solution. However, all of the presently known complexes of this type decompose in a wet environment as solids and more rapidly in aqueous solution. The rate of decomposition depends upon the particular macrocyclic ligand and also the nature of the axial ligands present. Water is not unique in causing this decomposition as most solvents which are more basic than acetonitrile will induce rapid decomposition. It seemed to us that an understanding of the mechanism of this decomposition would be important for the study of these complexes as oxidizing agents and that it might permit the design of new trivalent complexes which were less suceptible to decomposition in basic solvents. Also we were aware that trivalent complexes are formed prior to oxidation of coordinated amines in iron(II),[6] nickel(II),[7] and ruthenium(II)[8] complexes and that ligand radical intermediates had been postulated as intermediates in these processes. A radical intermediate was proposed (but not observed) in the decomposition of a Cu(III)–tetramine complex which produced Cu(II) complexes containing imine donors.[3] A detailed study of the decomposition of analogous Ni(III) complexes where "long-lived" intermediates were observed might permit detection of such a species, if indeed it was formed.

For the mechanistic investigation we chose complexes **2** (meso isomer) and **4** as representative of this class of Ni(III) complexes. These are conveniently prepared from **1** and **3**, respectively by oxidation with $NOClO_4$ in acetonitrile.

The results of this study will show that a novel mechanism of decomposition (reduction) exists for these complexes which involves, in the first step, base promoted intramolecular oxidation of a coordinated amine donor with for-