Figure 2. ORTEP drawing of $PtOs_5(CO)_{16}(\mu\text{-}H)_6$ (**2**) showing 50% probability thermal ellipsoids. Selected intramolecular distances (Å): Pt-Os(1) = 2.689 (1), Pt-Os(2) = 2.664 (2), Pt-Os(3) = 2.684 (1), Pt-Os(4) = 2.703 (2), Pt-Os(5) = 2.954 (2), Os(1)-Os(2) = 2.912 (2), Os(1)-Os(3) = 2.858 (1), Os(2)-Os(3) = 2.911 (1), Os(4)-Os(5) = 2.870 (2).

the spectrum shows three resonances: (1) -9.73 ppm (d, 2 H), J_{H-H} = 2.1 Hz; (2) -17.86 ppm (s, 3 H); (3) -19.66 ppm (t, 1 H), J_{H-H} = 2.1 Hz. Resonance 1 contains satellites due to large coupling to one platinum atom, $^1J_{Pt-H}$ = 714.4 Hz, and small coupling to a second platinum atom, $^2J_{Pt-H}$ = 19.5 Hz. Resonance 1 is thus assigned to the two equivalent hydride ligands H(4) and H(5) shown in Figure 1. Resonance 2 shows small coupling to one platinum nucleus, $^2J_{Pt-H}$ = 16.4 Hz, and is assigned to the three hydride ligands H(1)-H(3) shown in Figure 1. Resonance 3 shows weak coupling to platinum, $^2J_{Pt-H}$ = 24.3 Hz, and is attributed to H(6). These assignments are also consistent with the small H-H couplings.

An ORTEP diagram of **2** is shown in Figure 2.[8,10] The cluster can be viewed as a vertex-shared, Pt, fusion of one tetrahedral $PtOs_3$ group to a triangular $PtOs_2$ group. The Pt-Os lengths to the Os_3 triangle are similar to those in **1**, but the Pt-Os(4) distance is unexpectedly short, 2.703 (2) Å, even though it contains *two* bridging hydride ligands. The Pt-Os(5) distance is long, 2.954 (2) Å, as expected since it contains one bridging hydride ligand. The existence of six bridging hydride ligands (located crystallographically, but not refined) was established by ^1H NMR spectroscopy. As in **1**, the spectrum of **2** at 25 °C in $CDCl_3$ shows three resonances: (1) -7.48 ppm (s, 2 H); (2) -12.17 ppm (s, 1 H); (3) -17.36 ppm (s, 3 H). Resonance 1 is assigned to H(4) and H(5), on the basis of large coupling to platinum, $^1J_{Pt-H}$ = 653.6 Hz. Resonance 2 is assigned to H(6), $^1J_{Pt-H}$ = 573.2 Hz, and resonance 3 to H(1)-H(3) on the basis of the small coupling to platinum, $^2J_{Pt-H}$ = 22.4 Hz.[11]

Electron counting shows that compound **2** is electron deficient by the amount of two electrons. It contains a total of 88 valence

Scheme I
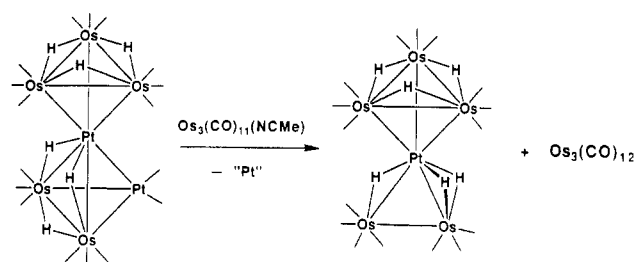
electrons, which is 2 less than the expected value of 90 based on Mingos' theory of condensed polyhedra (i.e. tetrahedron, 60 electrons, plus triangle, 48 electrons, minus shared vertex, 18 electrons).[12] We propose that this electron deficiency is associated with the *short* doubly hydride-bridged bond Pt-Os(4). A similar effect was observed in the well-known and studied 46-electron triangular cluster complex $Os_3(CO)_{10}(\mu\text{-}H)_2$ (**3**).[13] The unsaturation in **3** has been the site of remarkable reactivity that has permitted the synthesis of a wide variety of new compounds and even some examples of cluster catalysis.[13]

Although we have not yet identified the process by which **1** and **2** were formed, we have found that **1** can be converted to **2** in 20% yield by reaction with $Os_3(CO)_{11}(NCMe)$ (**4**); see Scheme I. The concomitant formation of $Os_3(CO)_{12}$ suggests that **4** is acting simply as a decarbonylation reagent. The fate of the platinum atom that was expelled from **1** in the course of this transformation has not yet been established.

We anticipate that **1** and **2** are only the first members of what will prove to be a much larger series of hydrogen-rich platinum-containing heteronuclear cluster complexes that may also exhibit some unusual reactivities.

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Inverse Experiments with Fluorine Detection

Since the publication by Freeman and Morris[1] on *J* polarization transfer between two coupled spin systems (the INEPT experiment), a great number of papers have appeared in the literature, dealing with proton-to-X polarization transfer (X = ^{13}C, ^{15}N). It was clear very rapidly that this kind of NMR experiment was very useful for inorganic chemists because of both the enormous sensitivity and experimental time gain when detecting low-γ nuclei. The second step was then to extend the INEPT scheme to transfer a phosphorus,[2] fluorine,[3] or carbon[4] polarization to another X magnetization. Accordingly, the so-called "inverse experiment"

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(10) Dark red crystals of **2** were grown from benzene/heptane solutions by slow evaporation of solvent at 25 °C. Crystal data: space group $P2_1/n$, a = 11.810 (4) Å, b = 15.656 (4) Å, c = 16.286 (6) Å, β = 109.15 (3)°, Z = 4. An empirical absorption correction was applied. The structure was solved by direct methods (MITHRIL) and was refined (2422 reflections) to the final values of the residuals R = 0.032 and R_w = 0.033.
(11) As with **1**, the equivalence of the three hydride ligands H(1), H(2), and H(3) may be the result of a dynamical averaging process. Further studies are in progress.
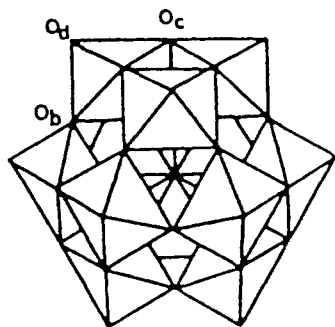
Figure 1. Structure of the polytungstate $(H_2W_{12}FO_{39})H_5$. Oxygens O_a, which are bound to three W, are not indicated in the figure; the fluorine atom replaces an O_a type oxygen.

Table I. Comparison between the Direct and the Indirect Determination of T_1 (^{183}W) for the Fluorinated Tungstens in $(H_2W_{12}FO_{39})H_5$ (0.3 M in D_2O)

	T_1	
	direct	indirect
T_1 value	1.79 s	1.78 s
	std dev 0.09	std dev 0.02
exptl time	3 days	1.3 h
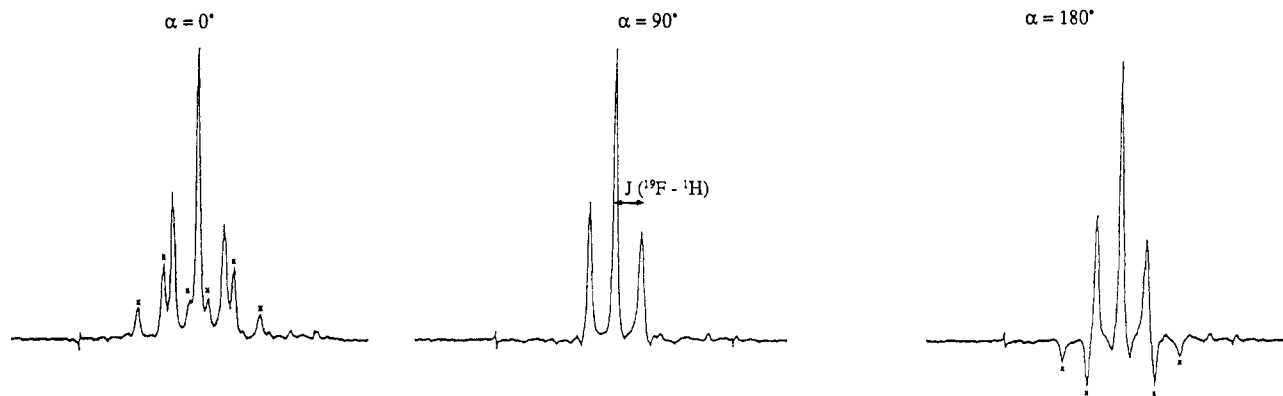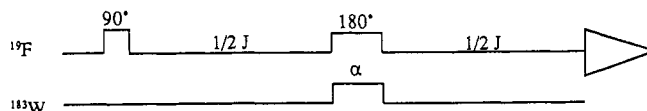
Figure 2. Determination of the 90°(^{183}W) pulse-width value by an echo type sequence. (sample: $(H_2W_{12}FO_{39})H_5$ (0.3 M in D_2O)). $^1/_2J$ was set to 0.0156 s for one scan; acquisition time = 1.44 s. 90° (^{19}F) pulse = 9.5 μs. The asterisks indicate the ^{183}W satellites.

first published by Maudsley[5,6] in 1977 is now practically a prerequisite for any elaborated low-γ isotope detection due to the sensitivity and information gain,[7] provided that a J scalar coupling exists. So far, inverse experiments with proton,[8] phosphorus,[2] and carbon detection[4] have been published. ^{19}F can also be a candidate of choice to start such an indirect scheme, and we report, in this communication, the first (^{19}F–^{183}W) and (^{19}F–^{13}C) inverse experiments. On the other hand, we shall demonstrate the use of the experiment for very low-sensitivity transition-metal T_1 measurements.

To check the validity of the method, we studied the polytungstate $(H_2W_{12}FO_{39})H_5$,[9,10] 0.3 M in D_2O, which is represented in Figure 1. For this analysis, the determination of the 90°(^{183}W) pulse-width value was done on the $(H_2W_{12}FO_{39})H_5$ sample itself by using an echo type sequence in which the 180° pulse acts as

a symetrizing operator with respect to the hetero (^{19}F–^{183}W) J coupling (Figure 2), allowing a clear-cut spectrum analysis. Figure 3 presents the inverse (^{19}F–^{183}W) 2D correlation of $(H_2W_{12}F-O_{39})H_5$. The pulse sequence used is the one proposed by Bodenhausen and Ruben.[11] This correlation easily detects the existence, in solution, of a second tungstate species (certainly the β isomer) barely detectable in the directly observed tungsten 1D spectrum.

Another important application of the inverse technique is the possibility of heteronuclear T_1 measurements.[12] Table I illustrates the comparison between the direct and indirect determination of the tungsten 183 T_1 relaxation time value in $(H_2W_{12}FO_{39})H_5$ and shows that the fit between the two methods is excellent. From the comparison between the two experimental times (72 versus 1.3 h), it is clear that the use of inverse DEPT sequence for such T_1 determination opens up new possibilities in heteronuclear magnetic resonance. As an example, chemical shift anisotropy contribution to relaxation pathway will be easily explored.

Finally, an extension of such inverse experiments with fluorine detection, could be the analysis of labeled metabolites in biological fluids via (^{19}F–^{13}C) correlation. The fluorine NMR spectroscopy of this class of compounds is very useful for detecting the end products of a drug model, through the metabolic pathway, blanking any protonated species, especially water. Of course, any

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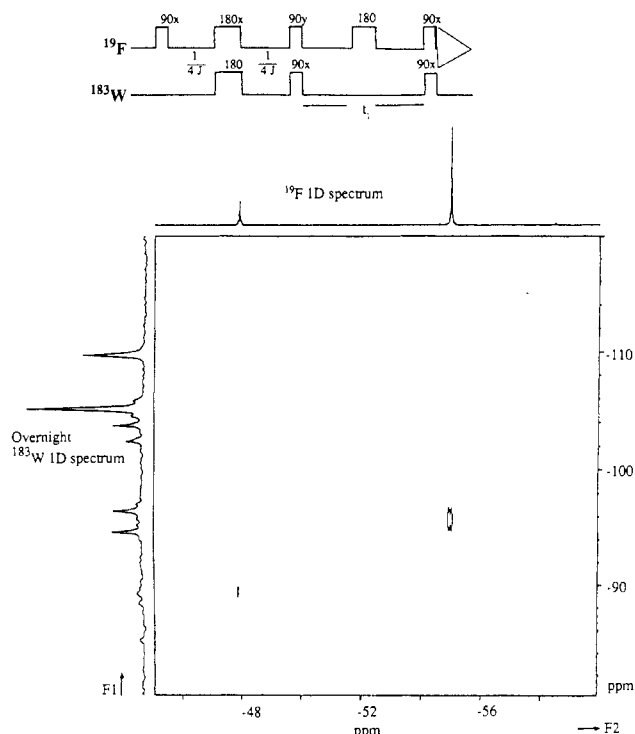(12) Sklenar, V.; Torchia, D.; Bax, A. *J. Magn. Reson.* **1987**, *73*, 375.

Figure 3. Magnitude model indirect (^{19}F–^{183}W) chemical shift correlation of $(H_2W_{12}FO_{39})H_5$ (0.3 M in D_2O). The spectrum results from a 64 × 4096 data matrix. The delay time between scans was 2 s, and the number of scans was 32. Spectral width in F2 = 5617.98 Hz. Spectral width in F1 = 667.56 Hz. Apodization was with a sine bell squared in both dimensions. The total acquisition time was 2 hours. The reference for chemical shift scaling in F1 is 2 M Na_2WO_4 in D_2O.
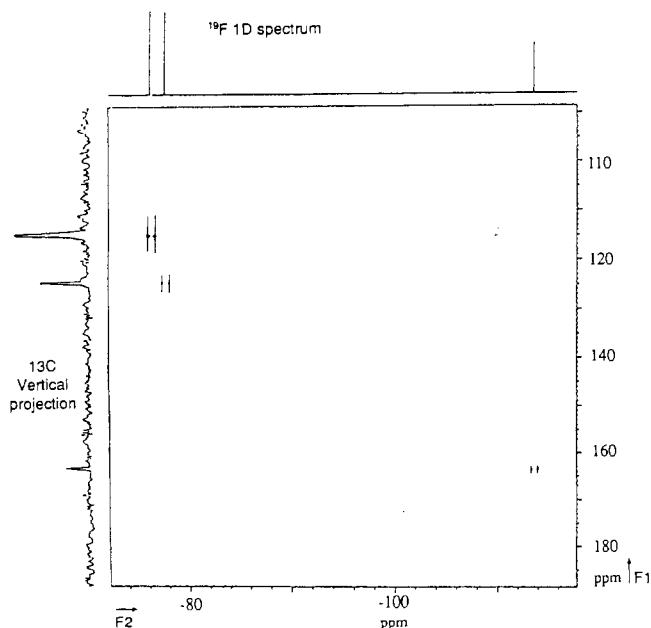

Figure 4. Magnitude mode multiple-quantum (^{19}F–^{13}C) chemical shift correlation of a mixture of fluorinated compounds in $CDCl_3$ (see text). The spectrum obtained with the four pulses sequence[14] results from a 256 × 8192 data matrix. The delay time between scans is 2 s, and the number of scans is 256. Spectral width in F2 = 17314.4 Hz. Spectral width in F1 = 10060.96 Hz. The spectrum was apodized by using an exponential multiplication of 2 Hz in F2 and 8 Hz in F1.

extra information that can be gained in such systems will be welcome for the biologist. Figure 4 is a good example of what can be done on a test mixture of 17 mM CF_3COOH, 20 mM CF_3CH_2OH, and 41 mM C_6H_5F in a $CDCl_3$ solution.

We clearly show that it is possible to extend easily the inverse experiments through the ^{19}F detection. From experimental time values comparison, it will be of particular interest for organo-

metallic/inorganic chemists to study the transition-metal center X of fluorinated iron, osmium, or rhodium species where a J-(^{19}F–X) coupling is present. On the other hand, it seems to be also a very promising NMR tool for low concentration fluorinated metabolite solutions.

Experimental Section. All the experiments have been run on an AM400 instrument equipped with a 5-mm inverse probe head. The proton channel of this probe head had been retuned at the fluorine frequency (376.4 MHz). The fluorine frequency had been generated by a BSV7 broad-band transmitter and the tungsten frequency (16.67 MHz) via a BSV3/BX accessory with a 200-W pulsed amplifier (3–66 MHz).

For the (^{19}F–^{13}C) experiment, the BSV3/BX accessory of the spectrometer has been equipped with a 150-W pulsed amplifier (5–122 MHz) and the determination of the 90°(^{13}C) pulse value has been done directly on the mixture of the fluorinated compounds via the standard procedure.[11]

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From Semiconductor–Semiconductor Transition (42 K) to the Highest-T_c Organic Superconductor, κ-$(ET)_2Cu[N(CN)_2]Cl$ ($T_c = 12.5$ K)

In this communication we report the discovery of an organic superconductor with the highest-T_c (12.5 K) recorded following the suppression of a semiconductor–semiconductor transition (42 K), which is accomplished by application of a minimal applied hydrostatic pressure (0.3 kbar). Comprehensive structure–property correlations for organic superconductors have been developed for the *isostructural* β-phase salts, β-$(ET)_2X$ ($X^- = I_3^-$, AuI_2^-, IBr_2^-).[1,2] Although several ambient-pressure superconductors are found in the κ-phase salts,[3,4] reliable structure-property correlations for these salts have not been developed due to the lack of *isostructural* κ-phase superconductors. The β- and κ-phase salts are characterized by very different structural packing motifs, viz., corrugated-sheet networks[5] of ET molecules and orthogonally arranged ET molecular dimers,[3] respectively. In this communication we report the discovery of a new κ-phase superconductor, κ-$(ET)_2Cu[N(CN)_2]Cl$, which is isostructural with the recently prepared ambient-pressure superconductor κ-$(ET)_2Cu[N(CN)_2]Br$ ($T_c = 11.6$ K)[4] and therefore has band dispersion relations and a Fermi surface[6] practically identical with those of κ-$(ET)_2Cu-[N(CN)_2]Br$.

Synthesis, ESR Spectroscopy, and Crystallographic Identification. The new superconductor, κ-$(ET)_2Cu[N(CN)_2]Cl$, was prepared in the same fashion as the isostructural Br salt.[4] The

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