

New Mass Spectra

Comparison of EI, FAB and DCI (electron capture mode) Mass Spectra of Hydrolytically Labile Dihalogenotitanium (IV) Porphyrins

Porphyrins and metalloporphyrins are widely used in various fields of chemistry and biomedical science (biomimetic chemistry, molecular catalysis, photosensitization, phototherapy, etc.).¹ Mass spectral studies are particularly useful for providing molecular weights, empirical formulas, and information about the substituent present in this class of compounds. We report here a comparison of several ionization techniques in the mass spectral analysis of dihalogenotitanium

(IV) tetraphenylporphyrins of formula $\text{TiX}_2(\text{tpp})$ (where $\text{X} = \text{F}, \text{Cl}$ or Br). These complexes have weak axial metal-ligand bonds that are readily hydrolysed to the oxotitanium (IV) complex $\text{TiO}(\text{tpp})$.²

Three ionization modes have been used: electron impact (EI), fast atom bombardment (FAB) and desorption chemical ionization (DCI). EI and FAB analyses were performed with a Kratos MS50 connected to a Finnigan MAT SS200 data system. The mass spectrometer resolving power was 2000. In EI, the electron energy was 70 eV and the samples were introduced with a direct inlet probe. In FAB, the samples dissolved

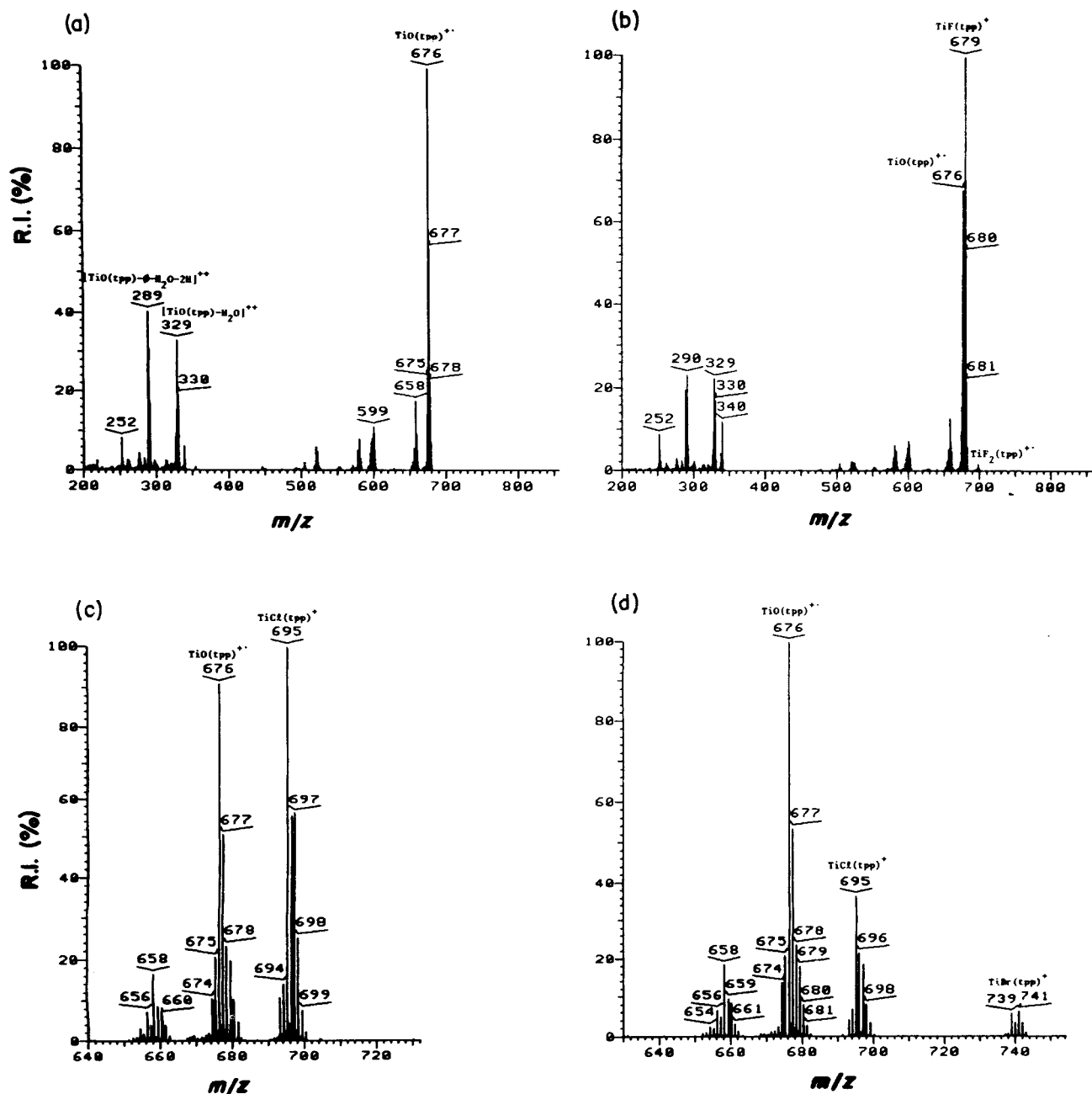
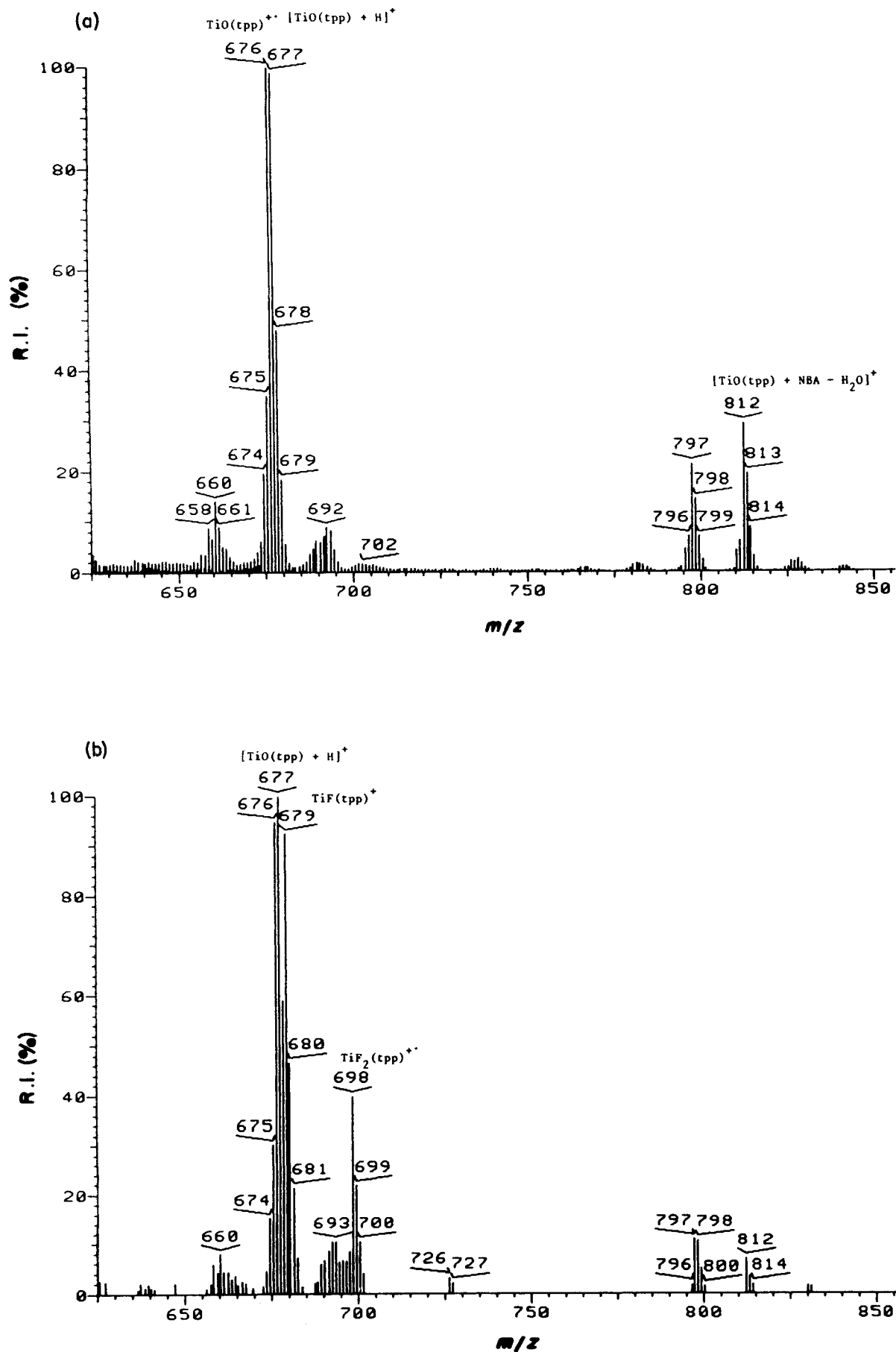


Figure 1. EI mass spectra of (a) $\text{TiO}(\text{tpp})$, (b) $\text{TiF}_2(\text{tpp})$, (c) $\text{TiCl}_2(\text{tpp})$ and (d) $\text{TiBr}_2(\text{tpp})$.

Figure 2. FAB mass spectra of (a) $\text{TiO}(\text{tpp})$ and (b) $\text{TiF}_2(\text{tpp})$.

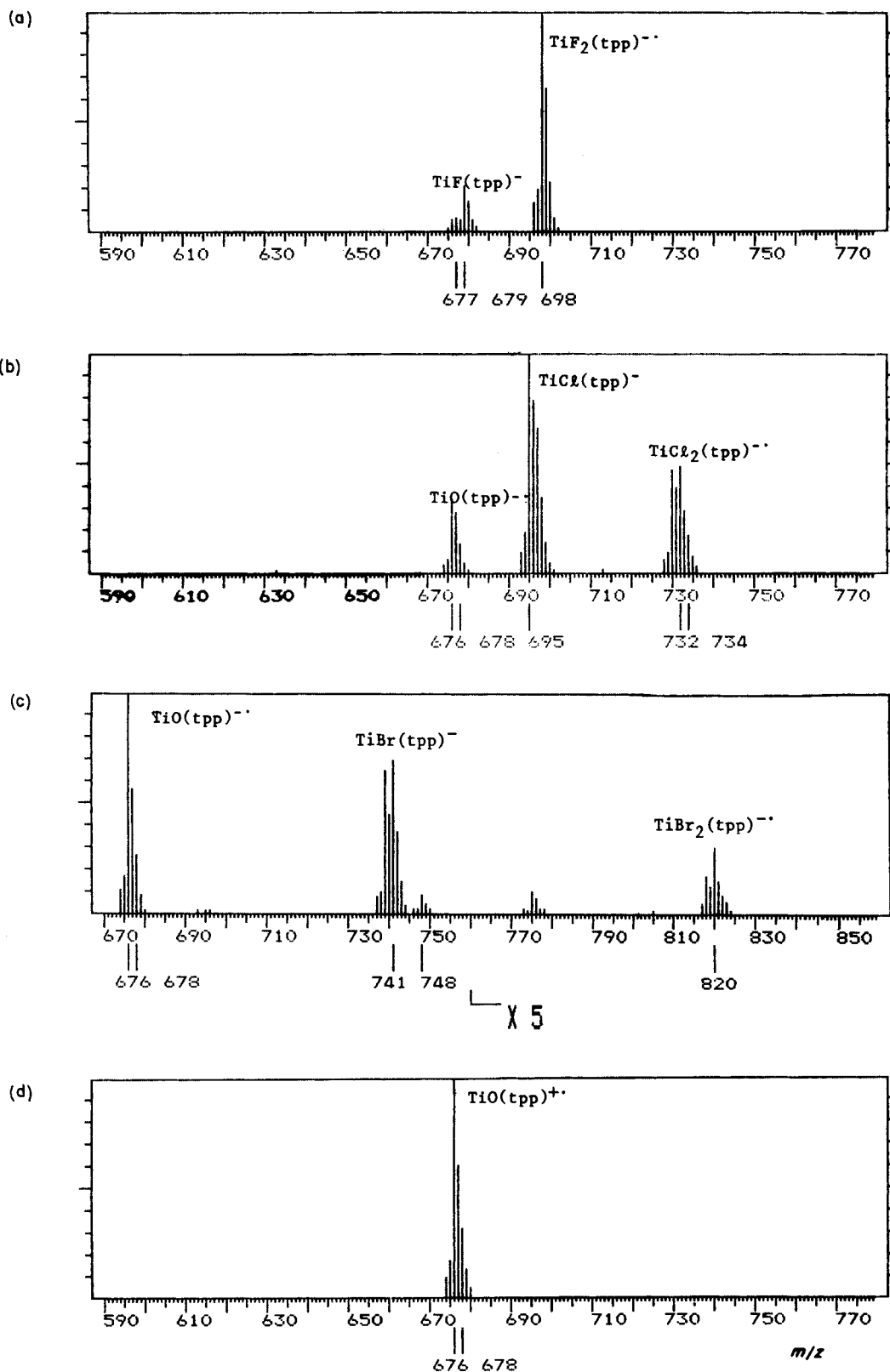


Figure 3. DCI (electron capture mode) mass spectra of (a) $\text{TiF}_2(\text{tpp})$, (b) $\text{TiCl}_2(\text{tpp})$, (c) $\text{TiBr}_2(\text{tpp})$. DCI (positive mode) mass spectrum of (d) $\text{TiO}(\text{tpp})$.

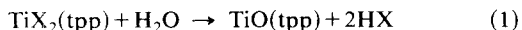
in a matrix were bombarded with xenon atoms of 8 keV (equivalent current of $20 \mu\text{A}$). The DCI mass spectra were obtained using a Riber R-1010 quadrupole (Nermag, France) coupled to a PDP 8/M (Digital Equipment). The filament on which the sample was deposited, was heated from 200 to 1000°C in 60 s (current programmed from 100 to 600 mA,

10 mA s^{-1}). The electron capture mode was used for all the compounds except $\text{TiO}(\text{tpp})$ which was analysed in the positive mode.

The EI mass spectrum of $\text{TiO}(\text{tpp})$ (source temperature 220°C) is shown in Fig. 1(a); it exhibits intense peaks of the molecular ion $[\text{TiO}(\text{tpp})]^{+\bullet}$ (main peak: m/z 676). The other

major peaks correspond to the loss of water (m/z 658), of one or more phenyl group (m/z 598, 520) and to doubly charged ions (m/z 329, 289).

The mass spectra of $\text{TiF}_2(\text{tpp})$ (250 °C), $\text{TiCl}_2(\text{tpp})$ and $\text{TiBr}_2(\text{tpp})$ (both 240 °C) (Figs 1(b), (c) and (d)) all exhibit important peaks corresponding to $\text{TiO}(\text{tpp})$ and to its fragments. This corresponds to the hydrolysis of the molecules according to reaction (1):



The molecular ions are not observed except for a very small peak for $[\text{TiF}_2(\text{tpp})]^{++}$. In contrast, the formation of $[\text{TiX}(\text{tpp})]^+$ (following loss of halide) is observed in every case. We also notice the presence of $\text{TiCl}_2(\text{tpp})$ as an impurity in $\text{TiBr}_2(\text{tpp})$ giving a rather important fragment ion $[\text{TiCl}(\text{tpp})]^+$ in the corresponding spectrum (Fig. 1(d)). Obviously, EI is not appropriate to get the molecular ions of this class of complexes.

In FAB, several matrixes have been tried, using in each case CHCl_3 as intermediate solvent. $\text{TiO}(\text{tpp})$ always exhibits important peaks of $[\text{TiO}(\text{tpp})]^{++}$ and $[\text{TiO}(\text{tpp}) + \text{H}]^+$ as shown in Fig. 2(a) with nitrobenzylalcohol (NBA) as a matrix. Addition products of the matrix with $\text{TiO}(\text{tpp})$ are also observed. The only formed fragment is $[\text{Ti}(\text{tpp})]^+$ (m/z 660). The spectrum of $\text{TiF}_2(\text{tpp})$ is shown in Fig. 2(b) with NBA as a matrix. Intense peaks corresponding to the hydrolytic product $\text{TiO}(\text{tpp})$ are again observed, but the molecular ion $[\text{TiF}_2(\text{tpp})]^{++}$ is well developed. NBA is the only matrix in which $\text{TiCl}_2(\text{tpp})$ and $\text{TiBr}_2(\text{tpp})$ could be dissolved, but they gave spectra typical of pure $\text{TiO}(\text{tpp})$.

Thus, it appears that the soft character of the FAB ionization technique is offset by hydrolysis or substitution reactions of the titanium complexes with the moist and/or hydroxylic liquid matrix.

In DCI (electron capture mode), we used a gas (NH_3 , 1 Torr) which does not act as a reagent gas (as in classical CI or DCI) but slows down the electrons. We get, in this way, electrons of low energy (a few eV) which stick to the desorbed molecules producing $\text{M}^{\cdot-}$ ions.³ The spectra of $\text{TiF}_2(\text{tpp})$ (Fig. 3(a)), $\text{TiCl}_2(\text{tpp})$ (Fig. 3(b)), $\text{TiBr}_2(\text{tpp})$ (Fig. 3(c)) have been obtained in this mode. The spectrum of $\text{TiO}(\text{tpp})$ obtained in the positive mode (reagent gas: NH_3) is shown in Fig. 3(d) for comparison. The molecular ion is the most abundant ion in the spectrum of $\text{TiF}_2(\text{tpp})$. Smaller peaks at masses 679 and 676 reveal the formation of $[\text{TiF}(\text{tpp})]^-$ and of $[\text{TiO}(\text{tpp})]^{--}$ in weak quantities. The spectrum of $\text{TiCl}_2(\text{tpp})$ shows a main peak for $[\text{TiCl}(\text{tpp})]^-$ with a molecular ion more abundant than the hydrolytic product $[\text{TiO}(\text{tpp})]^{--}$. The spectrum of $\text{TiBr}_2(\text{tpp})$ confirms the tendency (fluoride more stable than chloride more stable than bromide) observed in EI and in solution studies;² but the molecular ion can still be observed.

We can also notice that unlike the EI spectrum, the DCI spectrum (positive mode) shows no fragmentation. In the same way, the spectra of the halides show no fragmentation at masses lower than that of $\text{TiO}(\text{tpp})$. This confirms the soft ionization character of DCI. In fact, the electron capture mode, with its weak energy electrons, gives ions of low internal energy and consequently little fragmentation is observed. Incidentally, electron capture by these complexes of Ti(IV) gives anionic complexes of Ti(III) the stability of which has been demonstrated elsewhere.⁴ The success of DCI (electron capture mode) in providing intense molecular ions for this class of complexes is probably related to the chemical stability of the one-electron reduced compounds.⁵

These results suggest that DCI might constitute a significant development in the characterization by mass spectrometry of thermally and/or hydrolytically labile metal complexes and organometallic compounds. Investigation of other classes of complexes that exhibit a stable lower oxidation state will be necessary, however, before the generality of this observation can be demonstrated.

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