Comparison of **13** and **14** gives an external Δ_R value of −22.9 ppm.

In the case of the palladium complex **16**, the ^{31}P NMR resonance of the metalated ligand is shifted downfield from that of the unmetalated ligand.[25] This observation is in marked contrast to the corresponding platinum complex (**13**).[25] An explanation of the reversal for palladium cannot be offered at this time. Clearly, ^{31}P NMR data on the related complexes *cis*-$MC_6H_5(Cl)[P(OPh)_3]_2$ and *cis*-$M(C_6H_5)_2[P(OPh)_3]_2$ (M = Pd, Pt) would be helpful in understanding this anomaly. In fact, without related data of this type a suitable Δ_R value cannot be obtained for **16**. As in the case of the platinum analogue **13**, an internally derived Δ_R value from **16** is inappropriate since the metalated and unmetalated ligands have different trans groups.

Conclusions. The ^{31}P chemical shift of ortho-metalated triphenyl phosphite occurs at unusually low field compared to an *unmetalated* ligand having an equivalent stereochemical environment. This large downfield shift relative to unmetalated $P(OPh)_3$, as measured by Garrou's Δ_R parameter,[10] is characteristic of the ortho-metalated phosphite ligand in four-, five-, and six-coordinate complexes of a variety of transition metals. Values of Δ_R range from −22 to −49 ppm for the 10 complexes studied to date.

The theoretical origin of Δ_R in the present case, and in the case of five-membered chelate rings in general,[3–10] is not yet completely understood. Nevertheless, the lack of a theoretical justification for Δ_R does not diminish the usefulness of ^{31}P NMR spectroscopy for readily differentiating metalated and unmetalated phosphite ligands, even within the same complex. These observations lend strong support to our previous contention[2] regarding the applicability of this method for confirming ortho metalation in numerous related complexes.[28,29]

Note Added in Proof. Recently published ^{31}P NMR data[30] on several ortho-metalated ruthenium and rhodium complexes further support the conclusions drawn here.

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Registry No. **4**, 22289-58-3; **5**, 22008-86-2; **6**, 56474-44-3; **7**, 53532-85-7; ^{31}P, 7723-14-0.

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Reported Emission Spectrum of the $NiCl_4^{2-}$ Ion

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Sir:

Koester and Dunn[1] reported recently that the $NiCl_4^{2-}$ ion in $(Et_4N)_2ZnCl_4$ gave a well-resolved luminescence spectrum at 2.2 K. The spectrum was dominated by progressions in a vibrational mode of 825–835 cm^{-1} based on a number of electronic and vibronic origins. This interval was assigned as a C–C–N bending mode. An interval of about 919 cm^{-1} also appeared prominently. They suggested: "this system of the tetrachloronickelate negative ion and the tetraethylammonium cation is a unique example of an exciplex with a highly resolved emission spectrum". This explanation seemed unlikely and inconsistent with the interpretation of the absorption and emission spectra using crystal field theory. The luminescence spectrum was remarkably similar to those produced by complex ions containing the uranyl group[2] and the 830- and 919-cm^{-1} intervals are typical of the symmetric and antisymmetric stretching vibrations of the UO_2^{2+} entity.[2] It seemed possible therefore that the luminescence attributed to the $NiCl_4^{2-}$ ion by Koester and Dunn was caused by emission from a uranyl complex.

$(Et_4N)_2ZnCl_4$ and $(Et_4N)_2(Zn:Ni)Cl_4$ were prepared by the same methods as were used by Koester and Dunn, but we were unable to detect luminescence from either of these materials at 5 K using a range of ultraviolet and visible excitation frequencies. The same materials were then prepared by the same methods but adding uranyl nitrate (1 mol % relative to the zinc and nickel) to the ethanolic solution before the final recrystallization. The resulting crystalline powders luminesced strongly under 436-nm mercury excitation and in both cases the 5-K luminescence spectrum was almost identical with that reported by Koester and Dunn. The only significant

Table I. Comparison of the 5-K Luminescence Spectra[a] of $(Et_4N)_2ZnCl_4$ + UO_2^{2+} and $UO_2Cl_4^{2-}$ in the Range 20 055–19 040 cm^{-1}

$(Et_4N)_2ZnCl_4$ + UO_2^{2+}				$(Et_4N)_2UO_2Cl_4$[c]	$Cs_2UO_2Cl_4$[a,d]	Assignment
20 055[b]	*20 020*	*20 000*	*19 960*	19 994	20 097, 20 095	Origin (O)
	19 905	*19 885*		19 883	19 988, 19 979	O + $\delta(ClUCl)\epsilon_u$
19 800		*19 750*	19 751	19 751	19 856, 19 852	O + $\nu(UCl)\epsilon_u$
	19 750	*19 740*		19 732	19 849, 19 841	O + $\delta(OUO)\epsilon_u$
19 220	*19 185*	*19 165*	19 145	19 156	19 261, 19 258	O + $\nu(UO)\alpha_{1g}$
19 145	*19 100*	*19 080*	*19 040*	19 076	19 181, 19 167	O + $\nu(UO)\alpha_{2u}$

[a] Prominent bands only. [b] The italic bands correspond to features mentioned in ref 1. [c] This work. [d] Reference 2.

difference was that the weak band at highest energy was at 20 055 cm^{-1} in our spectra, about 20 cm^{-1} higher than the value reported previously. Most other bands agree within ±2 cm^{-1}, this being well within experimental error. The relative intensities of the 20 055-, 20 020-, 20 000-, and 19 960-cm^{-1} bands varied from sample to sample and also with temperature. This suggests that they are the electronic origins of four nonequivalent ions. To low energy of these origins are a number of vibronic origins involving vibrational frequencies of 115, 250, 260, and 920 cm^{-1} (Table I). At least six members of progressions in a mode of about 830 cm^{-1} based on these electronic and vibronic origins can be observed further to low energy. The values of the vibrational frequencies derived from the luminescence spectra may be compared with the 112 (ϵ_u), 238 (ϵ_u), 252 (ϵ_u), 831 (α_{1g}), and 916 cm^{-1} (α_{2u}) modes reported for $UO_2Cl_4^{2-}$ in $Cs_2UO_2Cl_4$.[3] Moreover, the observation of long progressions in the 830-cm^{-1} mode identifies this as a totally symmetric vibration whereas the other prominent vibrational intervals in the luminescence spectra must correspond to modes of odd parity. The agreement between these sets of vibrational intervals and the similarity of the luminescence spectra to those of $(Et_4N)_2UO_2Cl_4$ and $Cs_2UO_2Cl_4$ (Table I) suggest that the luminescent impurity in $(Et_4N)_2(Ni{:}Zn)Cl_4$ is the $UO_2Cl_4^{2-}$ ion or a very similar species.

Examination of the doped crystals under a X600 fluorescence microscope showed that the uranyl complex was evenly distributed throughout the crystals. The ease with which the $UO_2Cl_4^{2-}$ ion can be incorporated in $(Et_4N)_2ZnCl_4$ is unexpected but the anion size discrepancy may account for the presence of nonequivalent sites.

Registry No. $(Et_4N)_2UO_2Cl_4$, 59109-98-7; $(Et_4N)_2ZnCl_4$, 5964-74-9; UO_2^{2+}, 16637-16-4; $NiCl_4^{2-}$, 15320-56-6.

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