values are due to two and four electrons. Deviation from a 2:4 ratio is easily explainable on the basis of diffusion constant differences—$D_0$ for $Cu_2(BAA)_2$ would be expected to be slightly greater than that for $Cu_4(MOB)_2$. A reasonable interpretation of the CV shown in Figure 3 is that each binuclear unit undergoes the quasi-reversible, sequential transfer of two electrons at similar potentials and that the potential difference between the two units is on the order of 100–150 mV.

Unfortunately, CPE performed in the normal, preparative sense in pyridine is not very useful for studying this four-electron-transfer process. CPE at −1.10 V results in the addition of eight electrons and, obviously, the loss of all four Cu(II)'s from solution as Cu(Hg) amalgam. Similarly, CPE of $Cu_2(BAA)_2$ in pyridine at −1.20 V resulted in the addition of four electrons, whereas, in DMF/$Na^+$ 2 electrons were added at potentials corresponding to the two-electron CV wave.[4] Thus, although the CV and CA results for $Cu_2(BAA)_2$ in all three solvent environments are consistent with a two-electron-transfer process, the CPE results differ greatly. In pyridine two electrons per Cu(II) are added during CPE for both $Cu_2(BAA)_2$ and $Cu_4(MOB)_2$ in contrast to CV and CA results, which indicate only one electron per Cu(II). Thus, in pyridine, the conditions for bulk electrolysis (rapid stirring and greatly changing concentrations) cause a reaction or transformation that yields a species reducible at potentials more positive than −1.10 V. The simplest and, perhaps, most logical explanation is that the Cu(I) initially produced during CPE is lost from the complex and is present as $Cu(py)_x^+$. Further reduction of this species at the same potential yields (Cu(Hg) amalgam.

The loss of copper ions from $Cu_4(MOB)_2$ during CPE was monitored by analyzing the solution after the addition of each electron equivalent. The results are shown in Figure 4. If there were no secondary reactions during CPE, the plot should show 4 equiv of copper remaining in solution for each of 1, 2, 3, and 4 electron equiv added. Of course, after 4 electron equiv the current would be expected to drop to nearly 0 at the CPE potential applied. The fact that it does not is evidence for the importance of reactions that take place subsequent to the initial reduction of the Cu(II)'s to Cu(I)'s. The copper-containing product(s) of this reaction reduce at potentials more positive than −1.10 V. Thus, then they are formed, they are immediately reduced.

The results shown in Figure 4 indicate that even though there is decomposition under CPE conditions, a fair amount of the four-electron-reduced complex does exist after the addition of 4 equiv of electrons. After four electrons are added, less than one copper, on the average, has been lost from solution. If direct reduction to $Cu^0$ were occurring, then two coppers would be lost after four electrons were added. The simplest interpretation of these results is that when four electrons per molecule of $Cu_4(MOB)_2$ have been added the solution contains a mixture of species including the expected Cu(I) product, species with less then four copper's, and partially reduced Cu(II), Cu(I) species. Such a mixture would explain the facts that (1) four electrons per molecule have been transferred and (2) only about 3.2 equiv of the original 4.0 equiv of copper remain in solution. Subsequent addition of electrons beyond four result in the loss of 1 equiv of copper/equiv of electrons added.

## Summary

In unstirred solutions at a HMDE, the tetranuclear hexaketonate $Cu_4(MOB)_2$ exhibits electrochemical properties consistent with the transfer of four electrons at very similar potentials. This molecule contains two binuclear Cu(II) moieties separated by about 7 Å, each of which is structurally similar to the binuclear arrangement in bis(1,3,5-triketonato)dicopper(II) complexes. Since this binuclear unit is known to undergo sequential two-electron transfer in the triketonates, the four-electron transfer in $Cu_4(MOB)_2$ can be viewed as two two-electron transfers in noninteracting binuclear centers.

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**Supplementary Material Available:** A table of anisotropic thermal parameters and a table of hydrogen atomic parameters (5 pages); a table of structure factors (32 pages). Ordering information is given on any current masthead page.

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# Phosphorus Ylides as Hard Donor Ligands: Synthesis and Characterization of $MCl_4$(ylide-*O*)(THF) (M = Ti, Zr, Hf; Ylide = (Acetylmethylene)triphenylphosphorane, (Benzoylmethylene)triphenylphosphorane). Molecular Structure of *trans*-((Acetylmethylene)triphenylphosphorane-*O*)(tetrahydrofuran)tetrachlorotitanium(IV)–Tetrahydrofuran

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The reactions between oxophilic group 4 metal chlorides and the ambidentate $\alpha$-keto ylides (acetylmethylene)triphenylphosphorane (APPY) and (benzoylmethylene)triphenylphosphorane (BPPY), in THF, lead to the formation of O-bound transition-metal–ylide complexes. The compounds were characterized by proton, carbon-13, and phosphorus-31 NMR spectroscopy and by infrared spectroscopy. Crystallographic characterization of *trans*-[$TiCl_4$(APPY-*O*)(THF)]·THF (**4**) revealed that the ylide adopts the cisoid conformation in the solid state. **4** crystallizes in the monoclinic space group $P2_1/n$ in a unit cell of dimensions $a$ = 15.735 (5) Å, $b$ = 9.818 (3) Å, $c$ = 19.992 (5) Å, $\beta$ = 105.17 (2)°, and $V$ = 2981 (1) Å$^3$, with $R_F$ = 0.0554 ($R_{wF}$ = 0.0554) for 286 parameters and 2251 observed reflections having $F_o > 5\sigma(F_o)$. The potential of these complexes for forming O-bound, orthometalated species is discussed.

## Introduction

Our laboratory has long been interested in the coordination chemistry of ambidentate ligands.[1] One of our goals was to find an ambidentate ligand wherein control of the bonding mode (C vs O) would reside, at least in part, in variables that were found within the ligand itself.[2] The ease of systematic variation of the R, R′ and/or R″ groups in the phosphorus ylides of the type $R_3PCR'C(O)R''$ (**1**) suggested that these are ideal candidates.

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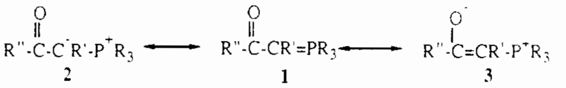
The keto-stabilized ligand can coordinate to a metal center through the ylide's methine carbon atom (**2**) or the carbonyl oxygen atom (**3**).



$$\text{R}''\text{-C}(=\text{O})\text{-C}^{-}\text{R}'\text{-P}^{+}\text{R}_3 \longleftrightarrow \text{R}''\text{-C}(=\text{O})\text{-CR}'{=}\text{PR}_3 \longleftrightarrow \text{R}''\text{-C}(\text{O}^{-}){=}\text{CR}'\text{-P}^{+}\text{R}_3$$

2 1 3

The first complex of one these ylides to be characterized by single-crystal X-ray analysis[3] involved bonding through the carbonyl oxygen to a hard Sn(IV) center in the trigonal-bipyramidal *trans*-[Sn($CH_3$)$_3$Cl(APPY-*O*)](APPY = (acetylmethylene)triphenylphosphorane, wherein $R = C_6H_5$, $R' = H$, and $R'' = CH_3$). Our initial efforts[4] were therefore directed toward the use of soft metal centers, such as Pt(II), Pd(II), and Hg(II), that would preferentially bond to the ylide's methine carbon. The resulting compounds were found[4b] to be either *trans*-[$MCl_2$(ylide-*C*)$_2$] (M = Pt(II), Pd(II)) or dinuclear [$Hg_2Cl_4$(ylide-*C*)$_2$]. Some years later, a single-crystal X-ray analysis of one of these complexes[5] showed that a dinuclear, C-bound, orthometalated species had formed ($[\overline{\text{Pt}(\mu\text{-Cl})\text{CH}_3\text{COCHP}(\text{C}_6\text{H}_4})(\text{C}_6\text{H}_5)_2]_2$). This reaction was intriguing and has led us to investigate the factors that influence orthometalation.[6-9] Other research groups have made significant contributions in this area, most notably those of Vicente[10] and Facchin.[11]

As part of these studies, we sought to prepare transition-metal complexes wherein the ylide would be bound through the carbonyl oxygen atom, allowing us to assess the influence of the metal atom in a reaction that could form an O-bound cyclometalated species. We had initially chosen Ni(II) and Co(II) as our hard metal centers and found[8] that reaction of the ylide with the anhydrous metal halides in acetonitrile led to protonation of the ylide to give $[\text{ylide-H}]_2^{+}[MCl_4]^{2-}$. Moreover, reactions[12] involving Ni(0) complexes and the ylide BPPY [BPPY = (benzoylmethylene)triphenylphosphorane, wherein $R = R'' = C_6H_5$ and $R' = H$] gave the new nickel $\widehat{\text{P O}}$ chelate complexes [Ni($PR_3$)($C_6H_5$)(($H_5C_6$)$_2$PCHC(O)($C_6H_5$))]. It was noted[12] that the nature of the nickel(0) complexes used resulted in phenyl group migration from the ylide to either the metal center or a hydrocarbon ligand, thus destroying the ylidic character of the ligand.

We then turned our attention to the more oxophilic group 4 metals, Ti, Zr, and Hf. The chemistry of early transition metals and ylides is mainly limited to cyclopentadienylmetal complexes and ylides of the type $R_3P{=}CR'R''$ (R, R', R'' = H, alkyl, aryl).[13-15] We felt that the coordinatively unsaturated metal halides would offer a ripe site for O-bonding of the α-keto ylides APPY and BPPY. We now report the preparation and characterization of the complexes $MCl_4$(ylide-*O*)(THF) (M = Ti, Zr, Hf; ylide = APPY, BPPY; THF = tetrahydrofuran) and the molecular structure of the carbonyl oxygen-bound *trans*-[$TiCl_4$(APPY-*O*)(THF)]·THF complex (**4**), as determined by a single-crystal X-ray diffraction study.

## Experimental Section

**General Procedures.** All reactions were carried out in a Vacuum Atmospheres drybox under a dinitrogen atmosphere. THF and diethyl ether were distilled from sodium benzophenone ketyl prior to use and stored under dinitrogen. All glassware was dried for 2 h (150 °C) prior to use. Metal halide salts were purchased and used as received from Aldrich Chemical Co. The ylides APPY and BPPY were prepared by a previously reported method.[16]

IR spectra were recorded on a Perkin-Elmer 283B infrared spectrophotometer as Nujol mulls between NaCl plates. Proton, proton-decoupled carbon-13, and proton-decoupled phosphorus-31 NMR spectra were obtained on a General Electric QE300 spectrometer operating at 300.17, 75.24, and 121.74 MHz, respectively. The proton and carbon-13 NMR spectra were referenced to residual solvent peaks and indirectly referenced to tetramethylsilane. The phosphorus-31 NMR spectra were referenced to external $H_3PO_4$ (85%). In all cases, positive chemical shifts are reported in parts per million downfield from the reference. Elemental analyses were performed by Micro-Analysis, Inc., Wilmington, DE 19808.

**Preparation of $TiCl_4$(APPY-*O*)(THF) (4).** A 100-mL round-bottom flask was charged with 1.05 mL of $TiCl_4$ (1 M solution in $CH_2Cl_2$) (1.05 mmol) and 40 mL of THF. To this yellow solution was added APPY (0.336 g, 1.05 mmol) in 10 mL of THF. The solution immediately turned orange. The solution was allowed to stir for 20 min, after which time the solvent was removed at reduced pressure to give an air- and moisture-sensitive orange solid (0.481 g, 79% yield). Anal. for $C_{25}H_{27}O_2PTiCl_4$. Calcd: C, 51.67; H, 4.69. Found: C, 48.61, 50.20; H, 4.82, 5.16. Satisfactory elemental analyses could not be obtained for this compound due to decomposition (usually within 7 days to a yellow or colorless powder under a dinitrogen atmosphere). Its decomposition products were not characterized.

**Preparation of $ZrCl_4$(APPY-*O*)(THF).** A 100-mL round-bottom flask was charged with 0.264 g of $ZrCl_4$ (1.13 mmol) and 40 mL of THF. To this colorless solution was added APPY (0.360 g, 1.13 mmol) in 15 mL of THF. The solution, which remained colorless, was stirred for 40 min. The solvent was removed at reduced pressure to give an air- and moisture-sensitive white solid (0.401 g, 57% yield). Anal. for $C_{25}H_{27}O_2PZrCl_4$. Calcd: C, 48.67; H, 4.37. Found: C, 47.58; H, 4.41.

**Preparation of $HfCl_4$(APPY-*O*)(THF).** A 100-mL round-bottom flask was charged with 0.330 g of $HfCl_4$ (1.03 mmol) and 40 mL of THF. To this colorless solution was added APPY (0.328 g, 1.03 mmol) in 15 mL of THF. The solution, which remained colorless, was stirred for 40 min. The solvent was removed at reduced pressure to give an air- and moisture-sensitive white solid (0.463 g, 63% yield). Anal. for $C_{25}H_{27}O_2PHfCl_4$. Calcd: C, 42.25; H, 3.83. Found: C, 42.03; H, 3.91.

**Preparation of $TiCl_4$(BPPY-*O*)(THF).** A 100-mL round-bottom flask was charged with 1.00 mL of $TiCl_4$ (1 M solution in $CH_2Cl_2$) (1.00

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**Table I.** Crystal Data for *trans*-$TiCl_4$(APPY-*O*)(THF)·THF (**4**)

(a) Crystal Data

| | | | |
|---|---|---|---|
| formula | $C_{29}H_{35}O_3PTiCl_4$ | $V$, Å$^3$ | 2981 (1) |
| fw | 652.17 | $Z$ | 4 |
| cryst syst | monoclinic | $D_{calc}$, g cm$^{-1}$ | 1.45 |
| space group | $P2_1/n$ | $\mu$, cm$^{-1}$ | 7.31 |
| $a$, Å | 15.735 (5) | $T$, K | 296 |
| $b$, Å | 9.818 (3) | cryst size, mm | 0.35 × 0.32 × 0.29 |
| $c$, Å | 19.992 (5) | color | orange |
| $\beta$, deg | 105.17 (2) | λ(Mo Kα), Å | 0.71073 |

(b) Data Collection

| | |
|---|---|
| scan type | Wyckoff |
| $2\theta$ limits, deg | 4–46 |
| max $h,k,l$ | ±18,+11,+22 |
| std rflcns (decay, %) | 3 std/197 reflns (40) |
| tot. no. of rflcns collcd | 4595 |
| no. of independent rflcns ($R_{int}$ = 2.11%) | 4160 |
| no. of obsd rflcns $F_o > 5\sigma(F_o)$ | 2251 |
| diffractometer | Nicolet R3m/μ |
| monochromator | highly oriented graphite |

(c) Structure Solution

| | |
|---|---|
| no. of least-squares params | 286 |
| data/param | 7.9 |
| $R_F$, % | 5.54 |
| $R_{wF}$, % | 5.54 |
| GOF | 1.225 |
| $g$, $w^{-1} = \sigma^2(F_o) + g(F_o)^2$ | 0.001 |
| $(\Delta/\sigma)_{max}$ | 0.017 |
| $(\Delta\rho)_{max/min}$, e Å$^{-3}$ | 0.392/−0.412 |

**Table II.** Atomic Coordinates (×10$^4$) and Isotropic Thermal Parameters (Å$^2$ × 10$^3$) for *trans*-$TiCl_4$(APPY-*O*)(THF)·THF (**4**)

| | $x$ | $y$ | $z$ | $U^a$ |
|---|---|---|---|---|
| Ti | 10324.6 (8) | 3839 (1) | 7143.4 (7) | 39.7 (5)* |
| P | 7855 (1) | 5568 (2) | 5480.1 (9) | 34.8 (7)* |
| Cl(1) | 11176 (1) | 5267 (2) | 6618 (1) | 60.8 (9)* |
| Cl(2) | 9814 (1) | 5756 (2) | 7597 (1) | 59.1 (8)* |
| Cl(3) | 9556 (1) | 2494 (3) | 7726 (1) | 73 (1)* |
| Cl(4) | 11054 (2) | 1915 (2) | 6878 (1) | 77 (1)* |
| O(1) | 9456 (3) | 3798 (5) | 6313 (2) | 41 (2)* |
| O(2) | 11409 (3) | 3894 (5) | 8057 (2) | 49 (2)* |
| C(1) | 11990 (7) | 5036 (11) | 8293 (5) | 103 (5)* |
| C(2) | 12657 (7) | 4628 (13) | 8915 (5) | 133 (6)* |
| C(3) | 12453 (8) | 3278 (10) | 9080 (6) | 120 (6)* |
| C(4) | 11757 (7) | 2744 (11) | 8510 (5) | 111 (5)* |
| C(5) | 9285 (4) | 3790 (7) | 5624 (4) | 38 (3)* |
| C(6) | 9848 (5) | 2864 (7) | 5313 (4) | 51 (3)* |
| C(7) | 8647 (4) | 4549 (7) | 5226 (4) | 37 (3)* |
| C(11) | 7146 (3) | 6257 (5) | 4110 (3) | 56 (3)* |
| C(12) | 6487 | 6318 | 3489 | 68 (4)* |
| C(13) | 5643 | 5844 | 3461 | 71 (4)* |
| C(14) | 5457 | 5309 | 4053 | 79 (4)* |
| C(15) | 6116 | 5248 | 4674 | 61 (4)* |
| C(16) | 6961 | 5722 | 4703 | 42 (3)* |
| C(21) | 7297 (3) | 3371 (4) | 6116 (2) | 57 (4)* |
| C(22) | 6947 | 2747 | 6612 | 65 (4)* |
| C(23) | 6769 | 3518 | 7146 | 54 (3)* |
| C(24) | 6940 | 4914 | 7183 | 59 (4)* |
| C(25) | 7290 | 5538 | 6688 | 47 (3)* |
| C(26) | 7468 | 4767 | 6154 | 34 (3)* |
| C(31) | 9148 (3) | 7453 (5) | 6076 (2) | 47 (3)* |
| C(32) | 9452 | 8751 | 6302 | 62 (4)* |
| C(33) | 8867 | 9845 | 6204 | 71 (4)* |
| C(34) | 7977 | 9641 | 5879 | 64 (4)* |
| C(35) | 7673 | 8342 | 5653 | 57 (4)* |
| C(36) | 8258 | 7248 | 5751 | 36 (3)* |
| Cs(1) | 5456 (23) | −82 (38) | 5634 (16) | 138 (10) |
| Cs(2) | 4710 (31) | −331 (50) | 5472 (23) | 168 (12) |
| Cs(3) | 5808 (22) | 292 (43) | 5156 (23) | 159 (12) |
| Cs(4) | 4821 (23) | 972 (41) | 5379 (18) | 150 (11) |
| Cs(5) | 4691 (33) | 1309 (51) | 4651 (26) | 197 (17) |
| Cs(6) | 5349 (43) | 1241 (62) | 5035 (33) | 230 (21) |

[a] Asterisk indicates equivalent isotropic $U$ defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

**Table III.** Pertinent Bond Lengths and Angles for *trans*-$TiCl_4$(APPY-*O*)(THF)·THF (**4**)

Bond Lengths (Å)

| | | | |
|---|---|---|---|
| Ti–O(1) | 1.854 (4) | P–C(7) | 1.774 (7) |
| Ti–O(2) | 2.150 (4) | C(5)–C(7) | 1.333 (9) |
| Ti–Cl(1) | 2.367 (3) | O(1)–C(5) | 1.332 (8) |
| Ti–Cl(2) | 2.322 (3) | C(5)–C(6) | 1.511 (11) |
| Ti–Cl(3) | 2.303 (3) | O(2)–C(1) | 1.446 (11) |
| Ti–Cl(4) | 2.343 (3) | O(2)–C(4) | 1.461 (11) |
| P–C(16) | 1.809 (5) | C(1)–C(2) | 1.457 (13) |
| P–C(26) | 1.799 (5) | C(2)–C(3) | 1.422 (16) |
| P–C(36) | 1.799 (5) | C(3)–C(4) | 1.456 (14) |

Bond Angles (deg)

| | | | |
|---|---|---|---|
| Cl(1)–Ti–Cl(2) | 89.3 (1) | O(1)–Ti–O(2) | 175.3 (2) |
| Cl(1)–Ti–Cl(3) | 176.2 (1) | Ti–O(1)–C(5) | 145.9 (4) |
| Cl(1)–Ti–Cl(4) | 90.5 (1) | Ti–O(2)–C(1) | 126.2 (5) |
| Cl(2)–Ti–Cl(3) | 89.2 (1) | Ti–O(2)–C(4) | 126.3 (5) |
| Cl(2)–Ti–Cl(4) | 169.2 (1) | C(7)–P–C(16) | 104.4 (3) |
| Cl(3)–Ti–Cl(4) | 90.3 (1) | C(7)–P–C(26) | 111.7 (3) |
| Cl(1)–Ti–O(1) | 89.2 (2) | C(7)–P–C(36) | 112.6 (3) |
| Cl(2)–Ti–O(1) | 96.8 (2) | P–C(7)–C(5) | 128.3 (6) |
| Cl(3)–Ti–O(1) | 94.5 (2) | P–C(16)–C(11) | 118.2 (2) |
| Cl(4)–Ti–O(1) | 94.0 (2) | P–C(26)–C(21) | 119.2 (1) |
| Cl(1)–Ti–O(2) | 87.0 (2) | P–C(36)–C(31) | 120.3 (2) |
| Cl(2)–Ti–O(2) | 85.8 (1) | O(1)–C(5)–C(6) | 116.5 (5) |
| Cl(3)–Ti–O(2) | 89.4 (2) | O(1)–C(5)–C(7) | 122.1 (7) |
| Cl(4)–Ti–O(2) | 83.5 (1) | | |

mmol) and 60 mL of THF. To this yellow solution was added BPPY (0.395 g, 1.10 mmol) in 20 mL of THF. The solution immediately turned orange. The solution was allow to stir for 20 min, after which time the solvent was removed at reduced pressure. The resultant orange oil was dissolved in 15 mL of diethyl ether and stirred for 10 min. The diethyl ether was removed under reduced pressure to give an air- and moisture-sensitive orange solid (0.329 g, 53% yield). Anal. for $C_{30}H_{29}O_2PTiCl_4$. Calcd: C, 56.10; H, 4.55. Found: C, 54.82; H, 4.57.

**Preparation of $ZrCl_4$(BPPY-*O*)(THF).** A 100-mL round-bottom flask was charged with 0.243 g of $ZrCl_4$ (1.04 mmol) and 50 mL of THF. To this colorless solution was added BPPY (0.400 g, 1.05 mmol) in 10 mL of THF. The solution, which remained colorless, was stirred for 1 h. The solvent was removed at reduced pressure to give an air- and moisture-sensitive white solid (0.421 g, 59% yield). Anal. for $C_{30}H_{29}O_2PZrCl_4$. Calcd: C, 52.56; H, 4.26. Found: C, 52.66; H, 4.45.

**Preparation of $HfCl_4$(BPPY-*O*)(THF).** A 100-mL round-bottom flask was charged with 0.444 g of $HfCl_4$ (1.39 mmol) and 40 mL of THF. To this colorless solution was added BPPY (0.530 g, 1.40 mmol) in 10 mL of THF. The solution, which remained colorless, was stirred for 45 min. The solvent was removed at reduced pressure to give an air- and moisture-sensitive white solid (0.602 g, 56% yield). Anal. for $C_{30}H_{29}O_2PHfCl_4$. Calcd: C, 46.62; H, 3.78. Found: C, 46.82; H, 3.96.

## X-ray Crystallography

**Experimental Details.** An orange crystal of **4** of good quality was mounted on a glass fiber with epoxy cement. Unit cell parameters were determined through least-squares refinement of 25 reflections ($20 \leq 2\theta \leq 25°$). Data were collected with a Nicolet R3m/μ diffractometer and Mo Kα radiation (λ = 0.71073 Å). No empirical absorption correction was necessary; however, a correction for a linear 40% decay in reflection intensity was applied to the data collected. Although the high decay likely results from loss of THF, it is apparently radiation induced; samples similarly coated with epoxy cement, but unirradiated, were unchanged for periods equivalent to the time of data collection. Crystal data are shown in Table I.

**Structure Solution and Refinement.** The structure was solved via direct methods, which located the Ti atom. The remaining non-hydrogen atoms were located through subsequent difference Fourier syntheses and least-squares refinement. All non-hydrogen atoms, except those in the solvent molecule, were refined anisotropically. Hydrogen atoms were calculated and fixed as idealized isotropic contributions ($d$(C–H) = 0.96 Å, $U = 1.2U$ of the attached carbon atom); phenyl rings were constrained to fit rigid hexagons ($d$(C–C) = 1.395 Å).

After all other non-hydrogen atoms were found, six peaks remained on a difference map (Cs(1)–Cs(6) in Table II). The six peaks, each peak having a thermal parameter typical of a carbon atom, formed a pseudoring structure. Although disorder within the ring could not be fully resolved, it was assumed to be a multiply positioned molecule of THF, the recrystallization solvent. The position of the oxygen atom was not determined. These atoms were then refined isotropically as carbon atoms.

Atomic coordinates are listed in Table II; pertinent bond lengths and angles are collected in Table III. All computer programs used in data

**Table IV.** Selected $^1H$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR Data for $MCl_4$(ylide-*O*)(THF)[a,b]

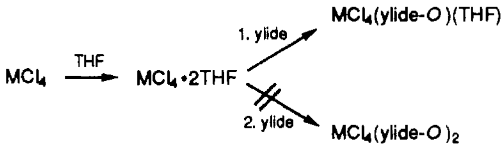
| compd | $\delta(CH)$[c,d] | $^2J(^{31}P-^1H)$[e] | $\delta(CH)$[c,d] | $^1J(^{31}P-^{13}C)$[e] | $^{31}P\{^1H\}$[c,d] |
|---|---|---|---|---|---|
| APPY | 3.52 (d) | 27.8 | 50.32 (d) | 108.7 | 16.33 (s) |
| $TiCl_4$(APPY-*O*)(THF) (4) | 5.17 (d) | 17.8 | 74.66 (d) | 97.0 | 13.91 (s) |
| $ZrCl_4$(APPY-*O*)(THF) | 5.01 (d) | 18.9 | 74.32 (d) | 99.5 | 13.92 (s) |
| $HfCl_4$(APPY-*O*)(THF) | 4.96 (d) | 18.9 | 74.46 (d) | 98.6 | 13.93 (s) |
| BPPY | 4.35 (d) | 25.5 | 49.19 (d) | 113.1 | 18.61 (s) |
| $TiCl_4$(BPPY-*O*)(THF) | 5.25 (d) | 21.6 | not found | | 15.24 (s) |
| $ZrCl_4$(BPPY-*O*)(THF) | 5.17 (d) | 16.1 | 76.47 (d) | 98.8 | 15.08 (s) |
| $HfCl_4$(BPPY-*O*)(THF) | 5.16 (d) | 16.0 | 76.54 (d) | 96.7 | 15.01 (s) |

[a] Ylide abbreviations: APPY = $H_3CC(O)CHP(C_6H_5)_3$; BPPY = $H_5C_6C(O)CHP(C_6H_5)_3$. [b] All spectra were obtained in THF-$d_8$. [c] $^1H$ and $^{13}C\{^1H\}$ peaks referenced to solvent signals and indirectly referenced to $Si(CH_3)_4$; $^{31}P\{^1H\}$ peaks referenced to external phosphoric acid (85%). [d] s = singlet; d = doublet. [e] Coupling constants are reported in Hertz.

collection, structure solution, and refinement are from the SHELXTL (version 5.1 G. Sheldrick, 1984) and P3 (Nicolet XRD, Madison WI) program libraries.

## Results and Discussion

The reaction between the group 4 metal halide salts and the $\alpha$-keto ylides APPY and BPPY in THF led to the desired formation of transition-metal complexes containing O-bound ylides. The complexes are thought to be formed by the displacement of one molecule of THF coordinated to the metal halide, as shown in eq 1. The use of more than 1 mol of ylide/mol of metal salt did not affect the product distribution, i.e., no $MCl_4$(ylide-*O*)$_2$ was detected.



(1)

M = Ti, Zr, Hf; ylide = APPY or BPPY

In these complexes, there are five potential bonding modes for each one of these ambidentate ylides: O-coordination, transoid or cisoid (with or without orthometalation), and C(methine)-coordination, with or without orthometalation. Simple C(methine)-coordination would produce a chiral center and the possibility of resolving optical isomers, as previously reported by using low-temperature NMR spectroscopy.[11a] Spectroscopic techniques such as IR and NMR spectroscopy enable one to distinguish between O-coordination and C(methine)-coordination.[4b,17] Selected proton, carbon-13, and phosphorus-31 NMR data are summarized in Table IV.

The proton NMR spectra (Table IV) indicate that the ylides are bound through the carbonyl oxygen. The $^2J(^{31}P-^1H)$ value resulting from the methine proton interaction with the phosphorus has been shown[17] to be a reliable indicator of the ylide's bonding mode. The coupling constants for the complexes are smaller than those observed for the free ylide and are close to those for confirmed[3,18a,b] ($^2J(^{31}P-^1H)$ = 24 Hz) and reported[17,18c,19] ($^2J(^{31}P-^1H)$ = 17–24 Hz) O-coordinated species. Compounds wherein the ylide is C-coordinated exhibit a $^2J(^{31}P-^1H)$ value of 6 or less Hz.[5-7,9,11a,20] Similar arguments can be made by using the $^1J(^{31}P-^{13}C)$ value resulting from the P–C(methine) interaction (Table IV). The trend is similar, following the pattern that the coupling constant is largest for the free ylide > O-coordinated ylide > ylide hydrohalide salt > C-coordinated ylide.

**Table V.** IR Data ($cm^{-1}$) for $MCl_4$(ylide-*O*)(THF)[a]

| compd | $\nu_{CO}$ | $\Delta\nu_{CO}$[b] |
|---|---|---|
| $H_3CC(O)CHP(C_6H_5)_3$ (APPY) | 1552[c] | |
| $TiCl_4$(APPY-*O*)(THF) (4) | 1530 | −22 |
| $ZrCl_4$(APPY-*O*)(THF) | 1535 | −17 |
| $HfCl_4$(APPY-*O*)(THF) | 1536 | −16 |
| $H_5C_6C(O)CHP(C_6H_5)_3$ (BPPY) | 1536[d] | |
| $TiCl_4$(BPPY-*O*)(THF) | 1520 | −16 |
| $ZrCl_4$(BPPY-*O*)(THF) | 1518 | −18 |
| $HfCl_4$(BPPY-*O*)(THF) | 1524 | −12 |

[a] Spectra obtained as Nujol mulls on NaCl plates. [b] $\Delta\nu_{CO}$ = $\nu_{CO}$ of compound − $\nu_{CO}$ of free ylide. [c] Reported as 1540 $cm^{-1}$; see ref 17. [d] Reported as 1520 $cm^{-1}$; see ref 4b.

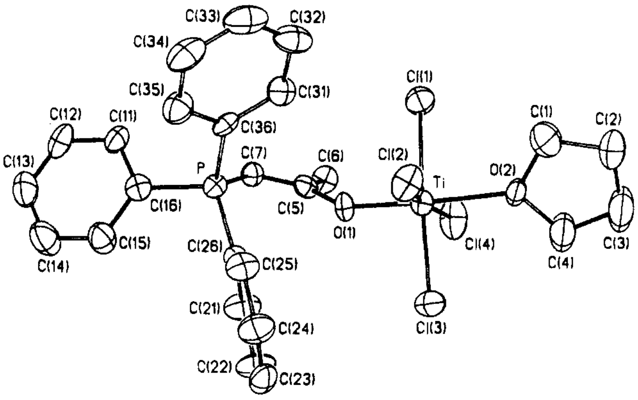


**Figure 1.** Molecular structure and labeling scheme for $TiCl_4$(APPY-*O*)(THF)·THF (4). Hydrogen atoms have been deleted. Thermal ellipsoids are shown at the 40% probability level.

The phosphorus-31 NMR data (Table IV) also serve as a good indicator of the ylide's bonding mode. When the ylide is O-coordinated, the phosphorus resonance is observed at slightly higher field, relative to the free ylide (usually within 4 ppm). However, there is a large shift (8–10 ppm) to lower field when the ylide is coordinated via the methine carbon. Resonances are observed to occur at slightly higher field for all the compounds, again pointing to O-coordination of the ylide.

The proton and phosphorus-31 NMR spectra indicate the presence of only one isomer in each of these O-coordinated group 4 ylide complexes, that being the cisoid isomer. The cisoid structure is, likewise, the only isomeric form exhibited by *trans*-[$Sn(CH_3)_3Cl$(APPY-*O*)], both in the solid state[3b] and in solution.[18a] Curiously, the other previously reported O-bound ylide complexes (those of Pd(II)[17] and W(0)[19]) have been found to occur predominately as the transoid isomer in solution. The transoid isomer would appear to be favored on steric grounds.

Infrared spectroscopy has been demonstrated to be another reliable indicator of the ylide's bonding mode.[4b,17,19,20a] Bonding through the carbonyl oxygen (where 3 is the major resonance contributor) leads to a decrease in the carbonyl stretching frequency, relative to that of the free ylide. Conversely, when the

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(18) (a) *trans*-$Sn(CH_3)_3Cl$(APPY-*O*) was prepared according to ref 3a and subjected to high-resolution NMR spectroscopy (proton, carbon, phosphorus). Only one isomer was detected. (b) Confirmed indicates X-ray crystal structure has been determined. (c) Reported indicates products have been spectroscopically identified (IR, NMR).

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**Table VI.** Comparison of Bond Lengths (Å) for Ylide Complexes

| compd | P⋯C[a] | C[a]⋯C[b] | C⋯O | ref |
|---|---|---|---|---|
| $[Sn(Me)_3(APPY\text{-}O)Cl]$[c,d] | 1.75 | 1.36 | 1.27 | 3 |
| $[TiCl_4(APPY\text{-}O)(THF)]\cdot THF$[c,d] (**4**) | 1.774 (7) | 1.333 (9) | 1.332 (8) | this work |
| $[PtCl(APPY)]_2$[c,e] | 1.762 (13) | 1.547 (22) | 1.228 (21) | 5 |
| *trans*-$[Pd(BBuPY)_2(Cl)_2]$[f,g] | 1.786 (5) | 1.478 (6) | 1.225 (7) | 7 |
| $[BPPY\text{-}H]_2[CoCl_4]$[h] | 1.806 (7) | 1.524 (11) | 1.220 (11) | 8 |
| $[BPPY\text{-}H]_2[NiCl_4]$[h] | 1.805 (6) | 1.515 (7) | 1.216 (7) | 8 |
| $[Pd_2(BBuPY)_2(Cl)_4]$[f,g,i] | 1.802 (7) | 1.503 (10) | 1.238 (10) | 9 |
| $[\{Au(PPh_3)\}_2\{\mu\text{-}C(PPh_3)CO_2Et\}]$[j] | 1.763 (10) | 1.464 (14) | 1.211 (13) | 10a |
| $[Ag(BPPY)_2][NO_3]$[f,h] | 1.757 (10) | 1.486 (15) | 1.240 (14) | 10b |
| $[Ag(CEPPY)_2][ClO_4]$[f,k] | 1.745 (17) | 1.466 (22) | 1.203 (20) | 10b |
| $[Ag_2\{\mu\text{-}\{\{CH(COOEt)\}_2PPh_2\}\}_2]$[f,l] | 1.771 (3) | 1.464 (4) | 1.209 (4) | 10e |
| $[Pd(Cl)(\eta^3\text{-}2\text{-}MeC_3H_4)(APPY)]$[c,f] | 1.769 (3) | 1.452 (5) | 1.228 (4) | 11a |
| $[Pd(CNR)(\eta^3\text{-}2\text{-}MeC_3H_4)(APPY)][BF_4]$[c,f,m] | 1.744 (9) | 1.46 (1) | 1.21 (1) | 11b |

[a] Methine or methylene carbon. [b] Carbonyl carbon. [c] APPY = $CH_3C(O)CHPPh_3$. [d] O-bound ylide. [e] C-bound ylide, with orthometalation. [f] C-bound ylide. [g] BBuPY = $(C_6H_5)C(O)CHP(n\text{-}C_4H_9)_3$. [h] BPPY = $(C_6H_5)C(O)CHPPh_3$. [i] Dinuclear species without orthometalation. [j] Methine carbon bridges two gold atoms. [k] CEPPY = $(H_5C_2O)C(O)CHPPh_3$. [l] Dinuclear, diylide complex. [m] R = $C(CH_3)_3$.

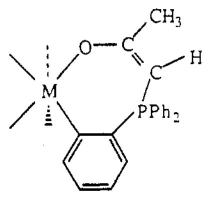
ylide is coordinated through the methine carbon (where **2** is the major resonance contributor), an increase in the carbonyl stretching frequency is observed. The IR data, summarized in Table V, indicate a shift to lower wavenumbers for the carbonyl stretching frequencies of all the complexes, clearly indicating that the ylides are O-bound.

Single crystals of **4** were obtained from the slow evaporation of a THF solution. Figure 1 shows the molecular structure of **4**. The slightly distorted Ti(IV) octahedron consists of four equatorial chlorines and two axial oxygen donors. This distortion [O(1)–Ti–O(2) = 175.3 (2)°; Cl(2)–Ti–O(1) = 96.8 (2)°; Cl(4)–Ti–O(2) = 83.5 (1)°] most likely arises from interactions between equatorial chlorines and the hydrogens of the coordinated THF molecule [Cl(1)⋯H(1a) = 2.750 Å; Cl(4)⋯H(4a) = 2.773 Å]. The nonbonding contacts of the chlorines to O(2) range from 2.994 to 3.134 Å. The Ti–O(2) distance of 2.150 (4) Å is in good agreement with those found for the previously reported structures $[TiCl_4\cdot THF]$,[21a] $[(TiCl_3\cdot 2THF)(\mu\text{-}O)]$,[21a] and the $[TiCl_5(THF)]^-$ anion.[21b]

The ylide is bonded through the carbonyl oxygen to the metal center and adopts the cisoid conformation; i.e., the $OTiCl_4(THF)$ fragment is cis to $P(C_6H_5)_3$ in the solid state. This is consistent with the results emanating from the solution studies. The Ti–O(1) distance is 1.854 (4) Å. No multiple-bond character can be assigned to the P–C(methine) bond, as evidenced by the long distance of 1.774 (7) Å (average P–C single-bond distance 1.81 Å[3b] versus the P⋯C distance in $Ph_3PCH_2$ of 1.66 Å, bond order 1.3[22]). The C(methine)–C(carbonyl) bond distance of 1.333 (9) Å indicates double-bond character, as would be expected in this bonding mode (see resonance structure **3** and the data in Table VI). The anticipated lengthening of the C–O bond is observed in the structure. The C–O bond distance for **4** is 1.332 (8) Å, which is considerably longer than the 1.27 Å reported for *trans*-$[Sn(CH_3)_3Cl(APPY\text{-}O)]$[3b] and is longer still than the C–O bond distances exhibited by the C-bound ylide complexes in Table VI.

**4** is the first O-bound transition-metal–ylide complex whose structure has been confirmed by a single-crystal X-ray diffraction study. There have been two other reported O-bound transition-metal–ylide complexes. Kawafune and Matsubayashi[19] reported the preparation of $W(CO)_5(BPPY\text{-}O)$ from the reaction between $W(CO)_5THF$ and 1 mol of BPPY. The proposed structure was based on proton NMR and IR data. Cationic palladium(II) complexes have been reported to contain the O-bound ylide APPY.[17] These proposed structures were also based on proton and phosphorus NMR and IR data.

As stated earlier, there are five potential bonding modes for these ylides. Crystallographic and solution studies of the group 4 transition-metal–ylide compounds indicate that the ylide adopts the O-bound, cisoid conformation. This suggests that an orthometalated species could be formed if the complexes were subjected to more forcing conditions. However, the inherent difficulty in the formation of a seven-membered metallacycle, such as **5**, would seem to rule out orthometalation.



**5**

If an O-bound, orthometalated complex were to form, it would involve the breaking of a group 4 metal–chlorine bond (bond energy 494 kJ/mol for Ti–Cl[23]) and a $C_6H_5$–H bond (bond energy 461 kJ/mol[23]) and require the formation of a group 4 metal–carbon bond (bond energy 429 kJ/mol for Ti–C[24]) with the simultaneous elimination of HCl (bond energy 432 kJ/mol[23]). Thus, the simple O-bound ylide complex would be favored over the orthometalated product by approximately 94 kJ/mol in the titanium complex. It is unlikely that the small increased contribution to $\Delta S$ (10 J/(K mol)[24]), caused by the elimination of HCl, could overcome this difference without a dramatic increase in temperature. Similar arguments can be made for the Zr and Hf complexes.

**Supplementary Material Available:** Tables of bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates, and complete NMR data (8 pages); a listing of structure factors (14 pages). Ordering information is given on any current masthead page.

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