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Heterodinuclear Titanium–Cobalt Complexes: Syntheses and Properties. X-ray Structure of $[({}^tC_4H_9O)_3TiCo(CO)_4]$ (Ti–Co)

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*Summary: An X-ray structural investigation establishes an unbridged Ti–Co bond in $[({}^tC_4H_9O)_3Ti{-}Co(CO)_4]$ (**1a**) and shows it to crystallize in the orthorhombic space group $Pbn2_1$, with $a = 1192.5(7)$ pm, $b = 1375.8(9)$ pm, $c = 1405.0(10)$ pm, and $Z = 4$. The variation of the alkoxide ligand leads to the more thermally unstable derivatives $[(RO)_3TiCo(CO)_4]$ ($R = i\text{-}C_3H_7$, $CH(CF_3)_2$, Ph), whereas trans-$[({}^tC_4H_9O)_3TiCo(CO)_3(PPh_3)]$ is formed in a selective axial carbon monoxide ligand substitution reaction between **1a** and triphenylphosphine.*

Heterodinuclear transition-metal complexes are of great interest for the study of synergistic effects found in bimetallic catalysis. In particular, early–late transition-metal complexes are widely regarded as models on a molecular scale for heterogeneous catalysts and have been studied in a variety of types of complexes with different combinations of early and late metals.[2] Up to now, metal–metal-bound titanium–cobalt complexes, which could serve as models for strong metal–support interaction (SMSI) catalysts,[3] have been rare. As part of our studies on unbridged early–late complexes which do contain the early transition metal in an oxide-like surrounding, we considered that titanium(IV) alkoxide units $Ti(OR)_n$ do represent a good model for the support component. Additionally, since they act as strong π-donors, alkoxide ligands may prevent the decomposition of heterobimetallic complexes in the course of a metal–metal bond homolysis reaction and reduction of Ti(IV).

Experimental Section

All reactions were carried out under an atmosphere of purified argon with the use of standard Schlenk techniques. Solvents were purified by standard methods and distilled under argon prior to use. Literature methods were used to prepare $[({}^tC_4H_9O)_3Ti{-}Co(CO)_4]$ (**1a**)[4] and $Na[Co(CO)_4]$.[5] The derivatives $Ti(OR)_4$ were commercial ($R = {}^tC_4H_9$, ${}^iC_3H_7$; Merck) or were prepared analogously to the literature method[6] but using toluene as a solvent. The chloro derivatives $ClTi(OR)_3$ ($R = {}^tC_4H_9$, ${}^iC_3H_7$, $CH(CF_3)_2$) were prepared by comproportionation reaction of 3 equiv of $Ti(OR)_4$ with $TiCl_4$ at elevated temperatures in toluene according to the literature method.[7] $ClTi(OPh)_3$ was prepared from $Ti(OPh)_4$ with $CH_3C(O)Cl$,[8] and attached CH_3COOPh was removed in vacuo at 150 °C. ^1H NMR spectra were obtained on a Tesla BS 587A 80-MHz instrument and ^{13}C NMR spectra on Bruker MSL 400 and Varian Gemini 300 spectrometers. Proton and carbon chemical shifts are referred to tetramethylsilane (δ 0.0 ppm) with positive shifts downfield of the reference. EI-MS measurements (70 eV, 50–400 °C) were performed on a Hewlett-Packard 5985W; IR spectra were recorded on a Carl Zeiss JENA MV 80 using 0.114-mm KBr or 0.4-mm CaF_2 cells. Microanalyses were done on a Carlo Erba 1106 elemental analyzer. Quantitative determinations of Ti and Co were carried out using the EDTA titrimetric method with (pyridylazo)naphthol indication and masking of Ti with NaF.

$[({}^iC_3H_7O)_3TiCo(CO)_4]$ (1b). A 37.5-mL amount of a 0.15 M solution of $ClTi(O^iC_3H_7)_3$ (5.59 mmol) in toluene was treated with 1.085 g (5.59 mmol) of $Na[Co(CO)_4]$ at −40 °C. The solution was warmed up within 1.5 h by stirring and reacted at room temperature for the same time. Filtration and evaporation of the solvent in vacuo yielded a red oil, which crystallized spontaneously after brief cooling with dry ice and was found to be spectroscopically pure by means of NMR. Yield: 2.03 g (92%). Anal. Calcd for $C_{13}H_{21}O_7TiCo$: C, 39.39; H, 5.30. Found: C, 38.75; H, 5.11. IR (toluene solution; ν(CO), cm^{-1}): 2058, 1994, 1962. ^1H NMR (toluene-d_8): δ 2.00 (d, 6 H, $CH(CH_3)_2$), 5.30 (m, 1 H, $OCH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (toluene-d_8): δ 205.1, 211.0 ($Co(CO)_4$); 80.8 ($OCH(CH_3)_2$); 27.2 ($OCH(CH_3)_2$). EI-MS: m/e 396 (0.5%, M^+), 284 (10%, $M^+ - 4CO$), 269 (100%, $M^+ - 4CO - CH_3$).

Formation of $[((CF_3)_2CHO)_3TiCo(CO)_4]$ (1c). A 10.55-mL amount of a 0.2 M toluene solution of $ClTi(OCH(CF_3)_2)_3$ (2.11 mmol) was diluted with 10 mL of the same solvent and treated with 415 mg (2.11 mmol) of $Na[Co(CO)_4]$ at −40 °C and the mixture stirred for 30 min at −30 °C. IR (ν(CO), cm^{-1}): 2085 (s), 2042 (s, br) 2003 (vs) for the bimetallic complex; 2069 (m), 2042 (s, br), 2023 (m), 1865 (w) for Co_2CO_8. Evaporation of the solvent at 0 °C led to the decomposition of the product.

Formation of $[(PhO)_3TiCo(CO)_4]$ (1d). In a manner analogous to that described above, $ClTi(OPh)_3$ was treated with the sodium cobaltate at −78 °C and the reaction mixture warmed to room temperature with stirring over 1 h. IR bands observed were as follows (cm^{-1}): 2116 (w), 2054 (vs), and 2026 (vs) for $HCo(CO)_4$; 2070 (s), 2012 (s), and 1966 (vs) + 1982 (vs) (symmetrically split band) for the bimetallic complex. These latter bands again disappeared within the next 30 min. A similar fast decomposition was observed at −30 °C.

***trans*-$[({}^tC_4H_9O)_3TiCo(CO)_3(PPh_3)]$ (2).** A 24.8-mL amount of a 0.195 M toluene solution of $[({}^tC_4H_9O)_3TiCo(CO)_4]$ (4.84

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mmol) was treated with 1.27 g (4.84 mmol) of solid PPh_3. The mixture was stirred for 14 h at room temperature *or* for 3 h at 50 °C; the CO evolved was allowed to leave the system. The completeness of the reaction was indicated by a change of color from red to yellow-brown and controlled by IR. The solvent was removed in vacuo at room temperature. The residue was stirred with 120 mL of hexane for 2 min; then the solution was filtered quickly. Immediate concentration of the solution to 10 mL by evaporating the solvent at 25 °C and cooling for 2 days at −78 °C gave well-shaped yellow crystals, which were filtered off, washed twice with 5-mL portions of cold hexane, and dried in vacuo. Yield: 2.87 g (86%). The product was recrystallized from hexane for the purpose of elemental analysis. It had to be stored at −20 °C. Anal. Calcd for $C_{33}H_{42}O_6PCoTi$: C, 58.96; H, 6.24; Co, 8.76; Ti, 7.12. Found: C, 58.21; H, 6.00; Co, 8.85; Ti, 7.29. ^1H NMR (C_6D_6): δ 1.54 (s, 27H, OC(CH_3)), 7.00 (m, 9 H, *m*- + *p*-H phosphine), 7.65 (m, 6 H, *o*-H phosphine). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 205.3 (Co(CO)$_3$), 136.74 (d, ^1J(CP) = 39.2 Hz), 133.45 (d, ^2J(CP) = 12.2 Hz), 129.80 (s), 128.02 (d, ^3J(CP) = 9.5 Hz). EI-MS: *m/e* 672 (0.3%, M^+), 588 (27%, $M^+ - 3CO$), 473 (100 %, $M^+ - 3CO - CH_3$).

X-ray Crystallography. To get crystals for the diffraction studies, 300 mg of **1a** was dissolved in 4 mL of hexane at −30 °C and the solution cooled immediately to −78 °C. Storage of the solution for 1 week at this temperature gave well-shaped colorless crystals which, in contrast to the product isolated from toluene, already decomposed above −40 °C. Therefore, all crystal manipulations were carried out while the material was kept under a cold nitrogen stream. A suitable crystal was mounted on a glass fiber with Vaseline and immediately transferred to a goniometer head on a Syntex P2$_1$ diffractometer equipped with a low-temperature device. Determination of the lattice parameters and intensity measurement were performed at −90(10) °C. The unit cell was determined from 15 reflections in the range $5 \le 2\theta \le 18°$, using graphite-monochromaed Mo Kα radiation. Intensities of reflections with $2\theta \le 50°$ were measured for $0 \le h \le 15$, $0 \le k \le 16$, and $0 \le l \le 16$ using the ω-scan technique. Two standard reflections were monitored every 100 reflections, and their intensities showed only random variations within 3.5%, for which no correction was made, indicating also that the compound did not undergo any decomposition during the measurement. Lorentz and polarization corrections were applied to the data, as well as an empirical absorption correction using the program DIFABS.[9] A total of 1578 data with $I \ge 2\sigma(I)$ was used for structure solution and refinement. The structure was solved by Patterson methods using SHELX-86,[10] refinement was done with SHELX-76,[11] and geometrical calculations were performed with PLATON.[12]

Systematic absences for $0kl$ with $k = 2n + 1$ and $h0l$ with $h + l = 2n + 1$ indicated the acentric space group *Pbn*2$_1$ (nonstandard setting of *Pna*2$_1$, No. 33) or the centrosymmetric space group *Pbnm* (nonstandard setting of *Pnma*, No. 62) as possible space groups. The structure was successfully solved in *Pbn*2$_1$. However, as the molecule exhibited an obvious mirror symmetry, refinement was also tried for space group *Pbnm*, assuming special positions (4c) on a mirror plane for the metal atoms, two CO groups, and O and two C atoms of one of the *tert*-butyl groups; this resulted in reasonable positions as well as temperature factors for the metal atoms and the atoms of the CO ligands, but the temperature factors of the carbon atoms of the *tert*-butyl groups became extremely high and the final *R* value was about 0.16. This led to the conclusion that, although the idealized symmetry of the molecule is C_s–*m*, the *tert*-butyl groups did not obey the mirror symmetry, thus destroying the C_s symmetry of the molecule.

Table I. Crystallographic Data for the Structure Determination of [($^t C_4H_9O)_3TiCo(CO)_4$]

formula	$C_{16}H_{27}O_7TiCo$
fw	438.20
cryst syst	orthorhombic
space group	*Pbn*2$_1$ (nonstandard setting of *Pna*2$_1$, No. 33)
a, pm	1192.5(7)
b, pm	1375.8(9)
c, pm	1405.0(10)
V, 10^6 pm^3	2305.1
Z	4
d_{calcd}, g cm^{-3}	1.26
cryst dimens, mm	0.4 × 0.4 × 0.6
μ(Mo Kα), cm^{-1}	10.9
radiation (Mo Kα), pm	71.069
scan mode	ω scan
scan speed, deg min^{-1}	1.50–29.30
$2\theta_{max}$, deg	50
abs cor	empirical,[a] min cor factor 0.777, max cor factor 1.250
no. of unique data	2987
no. of obsd data, $I \ge 2\sigma(I)$	1578
no. of refined params	283
R	0.078[b]
max shift/error	0.01[c]
max residual electron density, 10^{-6} e pm^{-3}	0.70

[a] DIFABS.[9] [b] $R = \sum(\|F_o - F_c\|)/|F_o|$. [c] For positional parameters of the atoms not belonging to the disordered *tert*-butyl groups.

The refinement was therefore continued in *Pbn*2$_1$ but constraints were imposed according to the assumed mirror symmetry to the $(CO)_4Co–TiO_3$ moiety and the $C(CH_3)_3$ groups were left unconstrained. This refinement coverged at *R* = 0.098. However, the temperature factors for C atoms of the *tert*-butyl groups were still rather high, indicating a certain degree of disorder of these groups, which is not uncommon.[13]

From a difference map two main orientations for one of the *tert*-butyl groups could be deduced and this group was refined subsequently with an occupancy factor of 0.5 for each of the orientations, but for the remaining two groups no split positions could be found, and the temperature factors of the C atoms belonging to these groups remained still very high. The structure was refined to an *R* value of 0.078. Because of errors in the positions of the *tert*-butyl C atoms, the geometry of these groups will not be discussed. The maximum shift/esd for the positional parameters of the atoms not belonging to the *tert*-butyl groups is 0.01, and the maximum residual electron density is 0.70 × 10^{-6} e pm^{-3}.

Results and Discussion

To our knowledge, up to now only for [$(CO)_9Co_3CO]_2CpTiCo(CO)_4$] was an unbridged titanium–cobalt bond confirmed by X-ray analysis;[14] other organyltitanium–cobalt carbonyls [$(C_6H_5CH_2)_3TiCo(CO)_3L$][15] could be studied in situ by low-temperature infrared and proton NMR spectroscopy only. As we have described briefly for [($^tC_4H_9O)_3TiCo(CO)_4$] (**1a**), the introduction of alkoxide ligands at Ti(IV) can cause compounds with a higher thermal stability.[4]

The structure of **1a** is shown in Figure 1. The most important feature of the compound is the covalent Ti–Co bond with a bond distance of 256.5(2) pm, which is slightly

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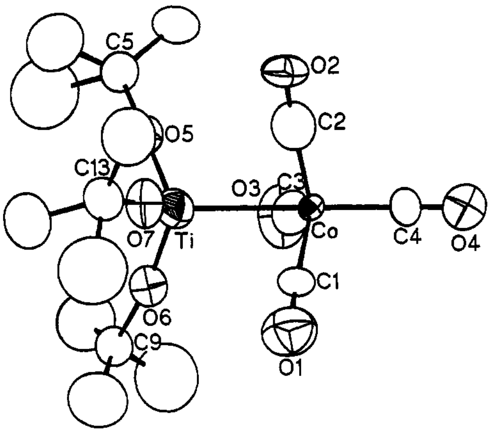

Figure 1. View of the structure of $[(^tC_4H_9O)_3TiCo(CO)_4]$, plotted by using ORTEP with 50% probability ellipsoids.

Table II. Selected Bond Distances (pm) for $[(^tC_4H_9O)_3TiCo(CO)_4]$

Co–Ti	256.5(2)	O(7)–C(13)	137(2)
Co–C(1)	175.9(7)	O(7)–C(13)′	133(2)
Co–C(2)	175.9(7)	C(5)–C(6)	155(2)
Co–C(3)	172(1)	C(5)–C(7)	167(2)
Co–C(4)	177(1)	C(5)–C(8)	135(2)
Ti–O(5)	174.3(5)	C(9)–C(10)	153(1)
Ti–O(6)	174.3(5)	C(9)–C(11)	142(2)
Ti–O(7)	173.8(9)	C(9)–C(12)	169(3)
O(1)–C(1)	115.9(8)	C(13)–C(14)	169(3)
O(2)–C(2)	115.9(8)	C(13)–C(15)	151(3)
O(3)–C(3)	118(1)	C(13)–C(16)	144(3)
O(4)–C(4)	117(1)	C(13)′–C(14)′	164(2)
O(5)–C(5)	145(1)	C(13)′–C(15)′	146(3)
O(6)–C(9)	136(1)	C(13)′–C(16)′	148(3)

Table III. Selected Angles (deg) for $[(^tC_4H_9O)_3TiCo(CO)_4]$

C(2)–Co–C(1)	114.3(5)	O(3)–C(3)–Co	177.5(9)
C(3)–Co–C(1)	118.0(3)	O(4)–C(4)–Co	171(1)
C(3)–Co–C(2)	118.0(3)	O(5)–Ti–Co	107.5(2)
C(4)–Co–C(1)	101.1(3)	O(6)–Ti–Co	107.5(2)
C(4)–Co–C(2)	101.1(3)	O(6)–Ti–O(5)	110.7(3)
C(4)–Co–C(3)	99.2(5)	O(7)–Ti–Co	109.4(3)
Ti–Co–C(1)	80.4(2)	O(7)–Ti–O(5)	110.8(2)
Ti–Co–C(2)	80.4(2)	O(7)–Ti–O(6)	110.8(2)
Ti–Co–C(3)	77.8(3)	C(5)–O(5)–Ti	169.5(7)
Ti–Co–C(4)	177.0(4)	C(9)–O(6)–Ti	169.5(8)
O(1)–C(1)–Co	177.7(7)	C(13)–O(7)–Ti	161.8(9)
O(2)–C(2)–Co	177.7(7)	C(13)′–O(7)–Ti	167.1(9)

longer than the sum of the covalent radii (250 pm). This distance is shorter than the value of 261.4 pm found for the Ti–Co bond in $[(CO)_9Co_3CO]_2CpTi-Co(CO)_4$. Both values are indicative of the crowded environment of the metal–metal bond. The coordination around the Co atom is trigonal bipyramidal; the Co–C distances vary between 172(1) and 177(1) pm and the C–O bond lengths between 116(1) and 118(2) pm. They agree with values found for other substituted cobalt carbonyls. The coordination around Ti is tetrahedral. Ti–O distances (about 174 pm) and Ti–O–C angles are in agreement with a certain amount of π-interaction between titanium and the alkoxide oxygen.[16]

Consistent with the spectroscopic data, in particular IR data,[17] there is no obvious structural evidence for a bridging character of the equatorial carbonyl ligands. The solid-state structure shows that there is no steric hindrance with respect to a rotation around the titanium–cobalt bond, which is consistent with the single resonances found in the ^{13}C NMR spectrum for the C atoms of the *tert*-butyl groups and the equatorial CO ligands, respectively. However, the bulkiness of the $(^tC_4H_9O)_3Ti$ fragment seems to hinder rotational exchange of the CO groups at the cobalt atom, because we have observed two ^{13}C resonances, at 201.8 and 203.6 ppm, which are clearly separated in the carbonyl region and assigned to the equatorial and axial CO groups, respectively.

Variation of the alkoxide ligands in **1a** is possible by using the salt elimination route. The stability of the derivatives formed depends remarkably on the type of the alkoxide which is introduced. Thus, a corresponding isopropoxy complex, $[(^iC_3H_7O)_3TiCo(CO)_4]$ (**1b**), was formed from $ClTi(O^iC_3H_7)_3$ and $Na[Co(CO)_4]$ in toluene. Very similar to **1a**, **1b** is first isolated as an red oil, which does crystallize spontaneously after short cooling and can be recrystallized from hexane as colorless crystals. As indicated by infrared spectroscopy, **1b** decomposes in solution with the formation of $HCo(CO)_4$; in toluene this reaction is faster, compared with that for **1a**. The IR bands observed at 1962 (vs), 1998 (s), and 2058 (s) cm^{-1} are consistent with the $(2A_1 + E)$ pattern of a metal carbonyl fragment of C_{3v} symmetry. In the ^{13}C NMR spectrum there are again two carbonyl resonances at 205.1 and 211.0 ppm, which is to some extent downfield compared with the *tert*-butoxy analogue. Electron impact mass spectrometry shows that the cleavage of the titanium–cobalt bond is no preferred fragmentation pathway. The most stable fragment is $\{[M^+] - 4CO - CH_3\}$ (*m/e* 269).

The analogous perfluoromethyl isopropoxy and phenoxy derivatives $[((CF_3)_2CHO)_3TiCo(CO)_4]$ (**1c**) and $[(PhO)_3TiCo(CO)_4]$ (**1d**) can also be observed clearly by low-temperature IR spectroscopy in toluene mixtures of the corresponding chlorotitanium precursor and $Na[Co(CO)_4]$. IR bands at 2085, 2042, and 2003 cm^{-1} (**1c**) and 2070, 2012, and 1982, 1966 (split E band) cm^{-1} (**1d**) confirmed the formation of bimetallic products. The observed shift of the CO stretching frequencies to higher wavenumbers is consistent with the electron-withdrawing effect of the phenoxy and fluoroisopropoxy groups introduced. Decreased pπ–dπ interaction between the alkoxide oxygen and titanium will modify Ti(IV) to be a better electron acceptor, and via Ti–Co bonding, obviously the π-donor ability of cobalt is decreased also. Neither complex could be isolated due to low thermal stability and decomposition at –30 °C in solution. Interestingly, decomposition of **1c** gives $Co_2(CO)_8$ as the initial carbonyl product, suggesting a homolytic Ti–Co bond splitting reaction. From **1d** $HCo(CO)_4$ is formed, as it is from **1a** and **1b**. Monitoring the decomposition of **1a** in deuterated toluene and cyclohexane by infrared spectroscopy showed that no $DCo(CO)_4$ is formed via C–D activation of the solvent. A heterolytic Ti–Co bond cleavage reaction, involving hydride abstraction from the alkoxide ligand, may be the favored decomposition reaction of the derivatives discussed here. The site of C–H activation may be the β-C atom, if one considers that the hydrogen at the α-position in the perfluoromethyl isopropoxide derivatives is not being attacked.

Attempts to introduce other alkoxide ligands by treatment of **1a** with the appropriate alcohol failed. Using 1–3 equiv of ethanol at room temperature led to the decom-

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[17] The IR pattern of **1a** is consistent with CO groups ligated terminally at a center showing C_{3v} symmetry: ν(CO) 2062 (s), 1998 (s), 1966 (vs) cm^{-1}.

position of the bimetallic complex and formation of $HCo(CO)_4$. In the same sense also secondary amines may act as proton sources and will destroy the Ti–Co linkage. Treatment of the ^tBuO derivative with 2 equiv of piperidine (pip) in toluene at room temperature gives quick precipitation of $pipH^+Co(CO)_4^-$ in 60% yield: ν(CO) 1896 cm^{-1} (THF). This reaction is similar to that of $R_3Si–Co(CO)_4$ derivatives with secondary amines described earlier, giving $HCo(CO)_4$ and silylamides as products.[18]

1a undergoes a clean substitution reaction of the axial CO group when it is treated with an equimolar amount of PPh_3 in toluene, finally giving the pale yellow, crystalline *trans*-[$(^tC_4H_9O)_3TiCo(CO)_3(PPh_3)$] (**2**). The complex shows two ν(CO) IR bands at 1924 (vs) and 1993 (w) cm^{-1}. This is comparable with the early results found for [$Br_3Sn–Co(CO)_3(PPh_3)$], which showed bands at 1999 (s) and 2056 (w) cm^{-1},[19] considering that $Ti(O^tC_4H_9)_3$ has less Lewis acid character compared to the Br_3Sn unit. Although **2** can be handled more easily for analytical purposes than the parent tetracarbonyl complex, nearly all of the triphenylphosphine complex is decomposed in ~0.1 M toluene solution after it is stirred for 24 h at room temperature. The only decomposition products determined by spectroscopy are $HCo(CO)_3PPh_3$ and [$OTi(O^tC_4H_9)_2]_2$.[20] These products correspond to that found for the thermal decomposition of **1a**, suggesting that the decomposition reaction pathways for both complexes are similar.

The investigations show clearly that unbridged Ti–Co bonding can be stabilized by selected alkoxide groups ligated to the titanium. The more significant π-donor character of *tert*-butoxide compared with the other alkoxide groups used may be responsible for the relatively high thermal stability of **1a**. The same effect may be responsible for the strong differences in decomposition temperatures between the $OCH(CH_3)_2$ and $OCH(CF_3)_2$ derivatives, respectively, if one takes into account that the steric demands of these alkoxide groups are comparable. Consequently, introduction of strong π-donating amido ligands at titanium should give more stable Ti–Co complexes. However, the introduction of more bulk alkoxy ligands such as neopentoxide seems necessary to prove also the influence of steric factors on the stability of this type of complex. Furthermore, the reactivity of complex **1a** and the nature of the thermal decomposition reaction of complexes **1** and **2** as well as the formation of other titanium–metal-bound complexes containing the tri-*tert*-butoxytitanium(IV) unit are being studied.

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Supplementary Material Available: Listings of positional parameters and equivalent and anisotropic temperature factors for **1a** (3 pages). Ordering information is given on any current masthead page.

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[20] IR data for $HCo(CO)_3PPh_3$: ν(CO) 2056 (w), 2050 (m), 1976 (s) cm^{-1}. EI-MS for [$OTi(O^tC_4H_9)_2]_2$: *m/e* 477 (M^+ + *t*-Bu), 421 (M^+ + H), 405 ($M^+ - CH_3$), 349 ($M^+ - CH_3 - {}^iC_4H_8$) (assignment fits with computer simulation and spectra of a reference probe).