substitution is associative[14,15] but not when it is dissociative,[5] is consequently seen. The smaller methyl groups permit the necessary compact transition state. The changes in the reactivity toward dissociative substitution are less marked. At 30 °C, the dissociative lability of *cis*-[$PtMe_2(Me_2S)_2$] is about twice that of the Me_2SO analogue. This is the opposite of what is observed in the diphenyl analogues, but there the enthalpies of activation differ so much from one to another that the relative reactivities will depend upon the temperature of the reaction. The marked difference between the activation parameters for the dissociation of Me_2SO and Me_2S from their diphenyl complexes is not observed for the dimethyl analogues, and while the displacement of Me_2S does have a larger value for ΔS^*, the difference is too small to be significant. The nucleophilic discrimination of the [$PtMe_2(Me_2SO)$] intermediate is somewhat greater than that observed for [$PtMe_2(Me_2S)$], but in the absence of data for phosphine nucleophiles (masked by the preponderant associative pathway), the range of nucleophilicity studied is too narrow for significant comment to be made.

It must be concluded, therefore, that the change from C_6H_5 to CH_3 does not greatly affect the ease with which the dissociative activation takes place and that the stabilization of the three-coordinate intermediate by interaction between Pt and the ortho hydrogens in the phenyl ring plays little, if any, part in promoting the dissociative nature of the process.

Acknowledgment. Financial support for this work from the Italian Ministry of Education is gratefully acknowledged.

Registry No. Bpy, 366-18-7; phen, 66-71-7; dppp, 6737-42-4; bpym, 34671-83-5; dppe, 1663-45-2; dpte, 622-20-8; *cis*-[$PtMe_2(Me_2SO)_2$], 70423-98-2; *cis*-[$PtMe_2(Me_2S)_2$], 87145-38-8.

Supplementary Material Available: Tables SI and SII, giving primary kinetic data (k_{obsd}/s^{-1} and k_{calcd}/s^{-1}) (10 pages). Ordering information is given on any current masthead page.

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Preparation and Characterization of Palladium(II) and Platinum(II) $OTeF_5$ Complexes

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Pentafluoroorthotellurate ($OTeF_5^-$), or teflate, first prepared in 1964 in the form of its conjugate acid $HOTeF_5$,[2] has been well characterized as a bulky pseudohalide.[3-5] Although it has an ionic radius larger than iodide,[6] the $OTeF_5$ radical possesses an electronegativity equal to that of fluorine.[7] However, while $OTeF_5$ has proven to be a versatile, bulky, fluorine-like substitute for binary main-group and high-valent transition-metal fluorides,[3-5] the $OTeF_5^-$ anion does not display fluoride-like properties. For example, the hydrogen bond strength in the $H(OTeF_5)_2^-$ anion is much weaker than that in bifluoride, HF_2^-.[8] Nevertheless, the electronic and structural properties of $OTeF_5^-$ are sufficiently different from those of other anions[9] that its potential as an unusual ligand for low-valent transition metals in organometallic complexes warrants exploration. Our first reports in this area detailed the preparation, characterization, and reactivity of metal carbonyl teflates such as $Mn(CO)_5(OTeF_5)$.[10] In this paper we report the synthesis and spectral characterization of $Pt(OTeF_5)_2(NBD)$ (NBD = norbornadiene) and $Pd(OTeF_5)_2(C_6H_5CN)_2$ and describe the molecular structure of the platinum complex.

Table I. Details of the X-ray Diffraction Study for $Pt(OTeF_5)_2(NBD)$

mol formula	$C_7H_8F_{10}O_2PtTe_2$
mol wt	764.42
space group	$P2_1/c$
unit cell	
a, Å	9.197 (2)
b, Å	14.842 (4)
c, Å	10.486 (3)
β, deg	93.78 (2)
unit cell vol, Å^3	1428.2 (5)
Z	4
calcd density, g cm^{-3}	3.56
cryst dimens, mm	0.08 × 0.30 × 0.125
data colln temp, °C	−130
radiation (λ, Å)	Mo Kα (0.71073)
monochromator	graphite
abs coeff, cm^{-1}	145.8
2θ range, deg	3.5–50
reflcns	$\pm h,k \geqslant 0,l \geqslant 0$
no. of reflcns with $I > 2\sigma(I)$	2171
total no. of reflcns measd	2793
scan type	θ–2θ
scan speed, deg min^{-1}	variable (2–30)
data/param ratio	10.9
R	0.0318
R_w	0.0460
GOF	2.475
g	2.1 × 10^{-4} (refined)
slope of normal probability plot	1.970

Experimental Section

The general air-free procedures for the handling of these reactive, hygroscopic compounds and for obtaining IR and NMR spectral data have been described elsewhere.[8,10,11] The compound [$AgOTeF_5(tol)_2]_2$ (tol = toluene) was prepared by published procedures.[12]

$Pt(OTeF_5)_2(NBD)$. Solid $PtCl_2(NBD)$[13] (0.479 g, 1.34 mmol) was stirred for 12 h at 22 °C with a dichloromethane solution (20 mL) of [$AgOTeF_5(tol)_2]_2$ (1.42 g, 1.34 mmol). The AgCl precipitate was removed by filtration and washed with dichloromethane. The washings were combined with the filtrate, and the solvent was removed under vacuum at 22 °C. The white solid was recrystallized from a minimum of dichloromethane (75% yield). ^1H NMR (CD_2Cl_2, 22 °C, Me_4Si internal standard): δ 1.64 (2 H, methylene), 4.55 (2 H, bridgehead), 5.58 (4 H, olefin); $J_{PtH(olefin)} = 69.8$ Hz. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 22 °C, Me_4Si internal standard): δ 49.5 (methylene), 68.6 (bridgehead), 76.1 (olefin); $J_{PtC(olefin)} = 136$ Hz. ^{19}F NMR (CH_2Cl_2, 22 °C, $CFCl_3$ external standard): AB_4X pattern (X = ^{125}Te, 7.0% natural abundance, I = $^1/_2$); δ_A −33.2, δ_B −39.7; $J_{AB} = 166$ Hz, $J_{BX} = 3662$ Hz. $^{125}Te\{^1H\}$ NMR (CH_2Cl_2, 22 °C, aqueous $Te(OH)_6$ external standard): XAB_4 pattern (A, B = ^{19}F); δ −107; $J_{XA} = 3185$ Hz, $J_{XB} = 3657$ Hz. $^{195}Pt\{^1H\}$ NMR (CH_2Cl_2, 22 °C, aqueous K_2PtCl_4 external standard): δ −2834 (broad singlet, $\Delta\nu_{1/2} = 66$ Hz).

$Pd(OTeF_5)_2(C_6H_5CN)_2$. This compound was prepared as above by using $PdCl_2(C_6H_5CN)_2$[14] in place of $PtCl_2(NBD)$. It crystallized from

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Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$)[a] for $Pt(OTeF_5)_2(NBD)$

atom	*x*	*y*	*z*	U_{iso}[b]
Pt	1266 (1)	4684 (1)	1607 (1)	14 (1)
Te1	−2121 (1)	4059 (1)	2437 (1)	18 (1)
Te2	2437 (1)	2714 (1)	82 (1)	19 (1)
O1	−980 (6)	4649 (4)	1364 (6)	24 (2)
O2	1111 (5)	3525 (4)	559 (5)	20 (2)
F1	−1492 (6)	2930 (4)	2031 (6)	46 (2)
F2	−3630 (5)	3962 (4)	1216 (5)	36 (2)
F3	−3330 (5)	3464 (4)	3497 (5)	39 (2)
F4	−2924 (7)	5091 (4)	3033 (6)	42 (2)
F5	−802 (6)	4072 (4)	3836 (5)	42 (2)
F6	1463 (6)	1747 (4)	724 (5)	38 (2)
F7	1456 (5)	2536 (4)	−1468 (5)	34 (2)
F8	3733 (6)	1874 (4)	−437 (5)	41 (2)
F9	3622 (5)	3556 (4)	−630 (5)	33 (2)
F10	3634 (5)	2768 (4)	1561 (5)	30 (2)
C1	3116 (8)	6175 (6)	1766 (8)	21 (2)
C2	3427 (9)	5189 (6)	1448 (8)	20 (2)
C3	3410 (8)	4696 (5)	2565 (7)	16 (2)
C4	3062 (9)	5382 (7)	3582 (8)	26 (3)
C5	1463 (9)	5606 (7)	3174 (8)	28 (3)
C6	1512 (9)	6094 (6)	2040 (8)	24 (3)
C7	3844 (9)	6244 (7)	3142 (8)	28 (3)

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] The equivalent isotropic *U* is defined as one-third of the trace of the $\mathbf{U}_{ij}$ tensor.

dichloromethane as orange needles in 95% yield. ^{19}F NMR (CH_2Cl_2, 22 °C, $CFCl_3$ external standard): AB_4X pattern; δ_A −33.9, δ_B −40.3; J_{AB} = 167 Hz. $^{125}Te\{^1H\}$ NMR (CH_2Cl_2, 22 °C, aqueous $Te(OH)_6$ external standard): XAB_4 pattern (A, B = ^{19}F); δ −118; J_{XA} = 3180 Hz, J_{XB} = 3670 Hz.

Crystallographic Study of $Pt(OTeF_5)_2(NBD)$. A colorless crystal of this compound was centered on a Nicolet R3m diffractometer. Centering of 25 reflections ($2\theta_{av} = 21.8°$) allowed least-squares calculation[15] of the cell constants listed in Table I, which also contains other details of the X-ray diffraction data collection and refinement. The intensities of all reflections were measured by θ–2θ scans. Control reflections (800, 0,16,0, 006) monitored every 97 reflections showed no significant changes in intensity throughout the data collection.

An empirical absorption correction was applied to the observed data, based on the intensity profiles for 11 reflections over a range of setting angles (ψ) for the diffraction vector. Transmission factors ranged from 0.573 to 0.272. Lorentz and polarization corrections were applied to the data.

The tellurium and platinum atoms were located by direct methods, and all other non-hydrogen atoms were located in difference Fourier maps. Subsequent refinement involved anisotropic thermal parameters for all non-hydrogen atoms. Neutral-atom scattering factors and anomalous scattering correction terms were taken from ref 16. Hydrogen atoms were positioned 0.96 Å from carbon atoms with calculated isotropic thermal parameters 1.2 times the equivalent isotropic thermal parameters of the carbon atoms to which they were attached. The weighted least-squares refinement converged, with the average shift/esd = 0.003 over the last four cycles.

In the final difference Fourier synthesis, the maximum electron density was 1.62 e $Å^{-3}$ in the vicinity of the platinum atom. The minimum was −1.48 e $Å^{-3}$. Analysis of variance as a function of Bragg angle, magnitude of F_o, reflection indices, etc. showed no significant trends.

Tables II and III contain a list of atomic positional parameters and equivalent isotropic thermal parameters and a list of bond distances and angles. Available as supplementary material are a stereoview of the unit cell packing diagram (Figure S-1) and lists of anisotropic thermal parameters for all non-hydrogen atoms (Table S-I), hydrogen atom positions and thermal parameters (Table S-II), and observed and calculated structure factors (Table S-III).

Table III. Bond Lengths (Å) and Bond Angles (deg) for $Pt(OTeF_5)_2(NBD)$[a]

Pt–O1	2.065 (5)	Pt–O2	2.042 (6)
Pt–C2	2.141 (8)	Pt–C3	2.152 (7)
Pt–C5	2.137 (9)	Pt–C6	2.150 (9)
Te1–O1	1.815 (6)	Te1–F1	1.831 (6)
Te1–F2	1.831 (5)	Te1–F3	1.847 (6)
Te1–F4	1.829 (6)	Te1–F5	1.841 (5)
Te2–O2	1.808 (6)	Te2–F6	1.843 (6)
Te2–F7	1.826 (5)	Te2–F8	1.832 (6)
Te2–F9	1.848 (5)	Te2–F10	1.843 (5)
C1–C2	1.533 (12)	C1–C6	1.526 (11)
C1–C7	1.553 (12)	C2–C3	1.382 (12)
C3–C4	1.523 (12)	C4–C5	1.541 (12)
C4–C7	1.554 (14)	C5–C6	1.396 (13)
O1–Pt–O2	83.0 (2)	O1–Pt–C2	157.7 (3)
O2–Pt–C2	106.6 (3)	O1–Pt–C3	159.3 (3)
O2–Pt–C3	106.7 (3)	C2–Pt–C3	37.5 (3)
O1–Pt–C5	98.3 (3)	O2–Pt–C5	162.4 (3)
C2–Pt–C5	78.7 (3)	C3–Pt–C5	66.9 (3)
O1–Pt–C6	98.1 (3)	O2–Pt–C6	159.5 (3)
C2–Pt–C6	65.9 (3)	C3–Pt–C6	79.2 (3)
C5–Pt–C6	38.0 (3)	O1–Te1–F1	95.3 (3)
O1–Te1–Fe2	92.7 (2)	F1–Te1–F2	90.1 (3)
O1–Te1–F3	178.3 (2)	F1–Te1–F3	85.1 (3)
F2–Te1–F3	85.7 (2)	O1–Te1–F4	94.0 (3)
F1–Te1–F4	170.6 (3)	F2–Te1–F4	90.0 (3)
F3–Te1–F4	85.5 (3)	O1–Te1–F5	96.4 (3)
F1–Te1–F5	89.6 (3)	F2–Te1–F5	170.9 (3)
F3–Te1–F5	85.2 (2)	F4–Te1–F5	88.8 (3)
O2–Te2–F6	93.7 (3)	O2–Te2–F7	92.3 (2)
F6–Te2–F7	89.3 (2)	O2–Te2–F8	178.0 (2)
F6–Te2–F8	85.4 (3)	F7–Te2–F8	86.0 (2)
O2–Te2–F9	95.1 (2)	F6–Te2–F9	171.3 (2)
F7–Te2–F9	90.5 (2)	F8–Te2–F9	85.9 (3)
O2–Te2–F10	96.6 (2)	F6–Te2–F10	90.2 (2)
F7–Te2–F10	171.1 (2)	F8–Te2–F10	85.1 (2)
F9–Te2–F10	88.6 (2)	Pt–O1–Te1	123.4 (3)
Pt–O2–Te2	133.2 (3)	C2–C1–C6	99.4 (7)
C2–C1–C7	101.0 (7)	C6–C1–C7	101.2 (7)
Pt–C2–C1	97.4 (5)	Pt–C2–C3	71.7 (5)
C1–C2–C3	107.9 (7)	Pt–C3–C2	70.8 (4)
Pt–C3–C4	96.0 (5)	C2–C3–C4	104.8 (7)
C3–C4–C5	101.0 (7)	C3–C4–C7	102.7 (7)
C5–C4–C7	101.1 (7)	Pt–C5–C4	96.1 (6)
Pt–C5–C6	71.5 (5)	C4–C5–C6	105.3 (7)
Pt–C6–C1	97.2 (5)	Pt–C6–C5	70.5 (6)
C1–C6–C5	106.7 (7)	C1–C7–C4	92.4 (7)

[a] Estimated standard deviations in the least significant digits are given in parentheses.

Results and Discussion

The $OTeF_5^-/Cl^-$ metathesis reaction between the Pd(II) and Pt(II) chloro complexes of this study and $[AgOTeF_5(tol)_2]_2$ afforded four-coordinate d^8 metal complexes that are thermally stable indefinitely. Other reactions using phosphine complexes of group 10 metals, such as $PtCl_2(PPh_3)_2$, $PdCl_2(dppm)$,[17] and $NiCl_2(dppe)$[17] did not afford stable products and precipitated metallic deposits. This behavior is attributable to a redox reaction between $OTeF_5^-$ and trivalent phosphines: we have found that $[N(n\text{-}Bu)_4^+][OTeF_5^-]$[8] in dichloromethane slowly (days) oxidizes PPh_3 to $OPPh_3$ (it is conceivable that metal ions would catalyze this reaction). Furthermore, an intramolecular redox reaction is the cause of the thermal instability of $P(OTeF_5)_3$: the compound slowly decomposes to tellurium metal[18] and a variety of phosphorus(V) species containing P–F bonds.[19] Thus, while teflate seems to be compatible with low-valent metals, including Pd(II) and Pt(II), it is not a suitable ligand for phosphine-containing complexes.

Information about the metal–oxygen bond in our complexes is available from vibrational and ^{19}F NMR spectra, as previously

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(15) Calculations for diffractometer operations were performed by using software supplied with the Nicolet R3m diffractometer. All structural calculations were performed on the Data General Eclipse S/140 computer in the X-ray laboratory at Colorado State University with the SHELXTL program library written by Professor G. M. Sheldrick and supplied by Nicolet XRD Corp.

(16) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

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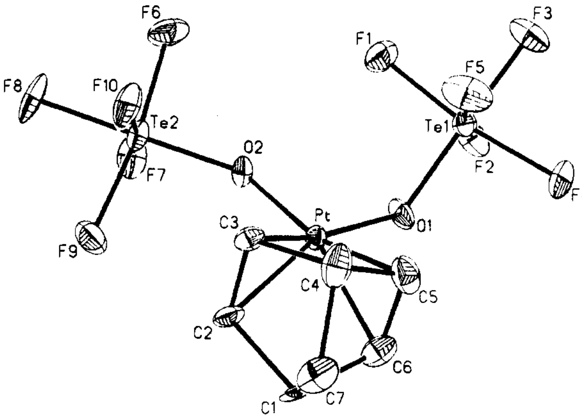

Figure 1. Drawing of the Pt(OTeF$_5$)$_2$(NBD) molecule (50% probability ellipsoids).

discussed.[8-12] For example, the Te–O stretching frequencies are 824 and 804 cm^{-1} for Pt(OTeF$_5$)$_2$(NBD) and 800 cm^{-1} (ν(TeO)$_{\text{asym}}$) for Pd(OTeF$_5$)$_2$(C$_6$H$_5$CN)$_2$.[20] These values are consistent with metal–oxygen bonds with a large degree of covalent character, in contrast to the "ionic" metal–oxygen bonds in Mn(CO)$_5$(OTeF$_5$) (848 cm^{-1})[10] and Fe(TPP)(OTeF$_5$) (849 cm^{-1})[21] (cf. [N(n-Bu)$_4^+$][OTeF$_5^-$], 867 cm^{-1} [8,9]). Similarly, the ^{19}F NMR chemical shifts of the axial fluorine atom in our metal teflates, δ_A −33.2 for Pt(OTeF$_5$)$_2$(NBD) and δ_A −33.9 for Pd(OTeF$_5$)$_2$(C$_6$H$_5$CN)$_2$, are midway between the extremes for ionic OTeF$_5^-$ (δ_A −19.0 for [N(n-Bu)$_4^+$][OTeF$_5^-$][8]) and a covalent teflate group (δ_A −42.4 for HOTeF$_5$[8]). No coupling between ^{195}Pt and ^{125}Te was observed in the ^{195}Pt or ^{125}Te NMR spectra of Pt(OTeF$_5$)$_2$(NBD); the bandwidths of the ^{125}Te resonances suggest that $^2J_{\text{TePt}}$ must be less than 50 Hz. This lack of coupling may be due to intermolecular exchange of OTeF$_5^-$ ligands that is fast on the NMR time scale. Two-bond coupling between tellurium and the central atom, M, in M(OTeF$_5$)$_x$ compounds is generally quite large: $^2J_{\text{TeTe}}$ = 1302 Hz in Te(OTeF$_5$)$_6$;[22] $^2J_{\text{TeXe}}$ = 1,008 Hz in Xe(OTeF$_5$)$_4$;[23] $^2J_{\text{TeAs}}$ = 420 Hz in As(OTeF$_5$)$_6^-$.[24]

The molecular structure of Pt(OTeF$_5$)$_2$(NBD) is shown in Figure 1. The teflate oxygen atoms and the centroids of the NBD double bonds adopt a planar arrangement about the platinum atom: the maximum deviation from the least-squares plane through O1, O2, Pt, and the two centroids is experienced by the Pt atom (0.016 Å). The small centroid–Pt–centroid bond angle of 70.7° is expected from the small bite of the NBD ligand.[25] However, the O1–Pt–O2 bond angle of 83.0 (2)° is surprisingly acute for two bulky, monodentate ligands. For example, the Cl–Pt–Cl bond angle in MCl$_2$(diolefin) complexes (M = Pt(II) or Pd(II)) varies from 90 to 95°.[25-27] Intermolecular contacts could conceivably be severe enough to be the cause of the small O1–Pt–O2 angle: the closest are F8···H3 (2.415 Å) and F1···C6 (2.894 Å). Both of these are shorter than the sum of the appropriate van der Waals radii, which are 1.20 Å for H, 1.70 Å for C, and 1.40 Å for F.[28] The closest intramolecular nonbonded contacts are also shorter than the sum of appropriate van der Waals radii: the closest are F10···H3 (2.250 Å) and F5···H5 (2.455 Å). Nevertheless, a stereoview of the unit cell packing (Figure S-1) suggests that the teflate groups could rotate away from these interactions without encountering other, more severe steric interactions. Thus, the small O–Pt–O angle is probably the result of an electronic effect, but steric effects cannot be ruled out and may contribute to this unusual structural feature.

The platinum–oxygen bond distances of 2.065 (5) and 2.042 (6) Å are near the high end of the recently reported range of 1.98–2.06 Å (a survey of 10 structures),[29] consistent with the accumulating evidence that teflate is a weak ligand (i.e. weaker than chloride but stronger than perchlorate or triflate).[10-12] When Pt(OTeF$_5$)$_2$(NBD) is dissolved in donor solvents such as acetone, acetonitrile, or nitromethane, OTeF$_5^-$, observed in IR and ^{19}F NMR spectra, dissociates from the metal complex to yield, presumably, Pt(OTeF$_5$)(NBD)(solvent)$^+$. The metal–carbon bond lengths, all equal to within experimental error (average 2.145 Å), are slightly shorter than those in PtCl$_2$(COD) (average 2.170 Å)[27] and PdCl$_2$(NBD) (average 2.162 Å).[25] Slightly stronger metal–olefin bonding in Pt(OTeF$_5$)$_2$(NBD) as compared with the bonding in these other complexes is also in harmony with metal–anion bonding being weaker for teflate than for chloride.

In summary, four-coordinate d^8 complexes of Pd(II) and Pt(II) with OTeF$_5^-$ ligands and without phosphine ligands have been prepared and are stable indefinitely. Some steric and/or electronic property of teflate gives rise to an unusually acute O–Pt–O angle in Pt(OTeF$_5$)$_2$(NBD). The unique properties of teflate suggest that it may be a useful ligand for catalytic complexes, for which subtle changes in ligand properties can have dramatic effects on catalytic activity.

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Supplementary Material Available: Figure S-1, giving a stereoview of the unit cell packing diagram, and Tables S-I and S-II, listing thermal parameters and hydrogen atom positions and thermal parameters (3 pages); Table S-III, a listing of calculated and observed structure factors (14 pages). Ordering information is given on any current masthead page.

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(20) Solid-state (Nujol mull) IR spectra of Pd(OTeF$_5$)$_2$(C$_6$H$_5$CN)$_2$ deserve further comment. Noncrystalline (powdered) samples produced by flash evaporation of solvent from benzene or dichloromethane solutions exhibited one band, at 800 cm^{-1}, in the ν(TeO) region. Assuming a trans geometry for this complex, this band is assigned to the asymmetric Te–O stretching vibration of the two trans Te–O oscillators. Crystalline samples from either solvent exhibited two bands in this region, at 819 and 788 cm^{-1}. Since either type of sample exhibited only one ν(CN) band at 2293 cm^{-1}, consistent with a trans geometry, we suggest that the splitting of the ν(TeO) band in the crystals is a solid-state effect.

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Synthesis and X-ray Structure of a Dimeric Rhenium(V) Compound: Re$_2$O$_3$Cl$_4$(3,5-Me$_2$pzH)$_4$·Me$_2$CO (pzH = Pyrazole)

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Polypyrazolylborate ligands form stable complexes with many transition metals in a wide range of oxidations states.[1] Recently, we demonstrated that an extensive series of mononuclear oxomolybdenum(V) complexes can be stabilized by the hydrotris(3,5-dimethyl-1-pyrazolyl)borate ligand, abbreviated HB-

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