Supplementary Material (3 pages)

Lithium, Titanium and Vanadium Dithiocarboxylates

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[2,6-$Mes_2C_6H_3CS_2$]$Li(Et_2O)_2$. A hemisphere of data was collected to 0.68 Å at 184 K. Final cell parameters were refined using 7123 reflections with I>10σ(I) from 26733 in the entire data set. Data were truncated to 0.80 Å during refinement due to poor agreement at higher resolution. Solution structure via direct methods in centrosymmetric space group $P2_1/n$ revealed the non-hydrogen structure. One molecule of [2,6–$Mes_2C_6H_3CS_2$]$Li(Et_2O)_2$ comprises the asymmetric unit. No other moieties are present. All non-hydrogen atoms, except atoms of the diethyl ether, were refined with parameters for anisotropic thermal motion. Hydrogen thermal parameters were set to 1.2 times the equivalent isotropic thermal parameter of the parent atom. Each of the coordinated diethyl ether groups is disordered. For each, a second orientation was modeled. Attempts were made to fit the ethers first as rigid bodies and second, with fixed interatomic distances. Neither of these models were satisfactory. In the end, only the distances between atoms C(30) and C(31) and also C(30') and C(31') were fixed. These vectors were restrained to 1.440(5) Å through the final stages of refinement. All other ether atoms refined freely. Thermal parameters for the ether atoms are somewhat large, reflecting this disorder. No significant features were present in the final difference electron density map.

[2,6-$Mes_2C_6H_3CS_2$]$TiCl_2(thf)_2 \cdot Et_2O$. A hemisphere of data was collected to 0.68 Å at 133 K. Final cell parameters were refined using 8414 reflections with I>10σ(I)

chosen from 36233 in the entire data set. Data were truncated to 0.73 Å during refinement due to poor agreement at higher resolution; 100% of the unique data was measured. Structure solution via direct methods in centrosymmetric space group $P2_1/c$ revealed the non-hydrogen structure. The asymmetric unit contains a molecule of diethyl ether and a molecule of the Ti complex. All non-hydrogen atoms were refined with parameters for anisotropic thermal motion. Hydrogen atoms were placed at calculated geometries and allowed to ride on the position of the parent atom. Hydrogen thermal parameters were set to 1.2 times the equivalent isotropic thermal parameter of the parent atom. No significant features were present in the final difference electron density map.

$[2,6\text{-}Trip_2C_6H_3CS_2]_2TiCl_2(py)_2$. A hemisphere of data was collected to 0.68 Å at 135 K. Final cell parameters were refined using 8316 reflections with $I>10\sigma(I)$ chosen from 56179 in the entire data set. Data were truncated to 0.77 Å during refinement due to poor agreement at higher resolution. Structure solution via direct methods in centrosymmetric space group P-1 (#2) revealed the non-hydrogen structure. The asymmetric unit contains a molecule of cocrystallized diethyl ether and a molecule of the Ti complex. All non-hydrogen atoms, excluding disordered atoms (described below), were refined with parameters for anisotropic thermal motion. Hydrogen atoms were placed at calculated geometries and allowed to ride on the position of the parent atom. Hydrogen thermal parameters were set to 1.2 times the equivalent isotropic thermal parameter of the parent atom. Hydrogen atoms were not added to disordered groups. No significant features were present in the final difference electron density map.

Two of the isopropyl substituents of a $2,6\text{-}TripC_6H_3C_S$ ligand were found to be disordered. Each of these were modeled over two positions as partial occupancy groups. For one minor component (C(54'), C(55'), C(56')), it was necessary to restrain bond lengths. The cocrystallized ether molecule was found to be disordered over two adjacent positions with approximately 0.6 and 0.4 occupancies. Attempts to model the disorder by fixing bond lengths proved unsatisfactory. The data were corrected for the disordered ether using Platon/SQUEEZE. This gave a calculated potential solvent area of 407.7 $Å^3$ (10.2% total volume) containing 79 electrons, which is consistent with ca. 1.9 molecules

of ether in the unit cell. The value of R1 (I>2σI) improved slightly (from 0.0660 to 0.0619) after the correction, and refinement of the model gave acceptable convergence. No significant features were present in the final difference electron density map.

[2,6-Trip$_2$C$_6$H$_3$CS$_2$]$_2$VCl(py)$_2$. A hemisphere of data was collected to 0.68 Å at 135 K. Final cell parameters were refined using 5363 reflections with I>10σ(I) chosen from 85590 in the entire data set. Data were truncated to 0.77 Å during refinement due to poor agreement at higher resolution. Structure solution via direct methods in centrosymmetric space group $P2_1/c$ revealed the non-hydrogen structure. The asymmetric unit contains two molecules of cocrystallized pyridine and a molecule of the V complex. All non-hydrogen atoms, excluding disordered atoms (described below), were refined with parameters for anisotropic thermal motion. Hydrogen atoms were placed at calculated geometries and allowed to ride on the position of the parent atom. Hydrogen thermal parameters were set to 1.5 times the equivalent isotropic thermal parameter of the parent atom for methyl groups and 1.2 times the equivalent isotropic parameter for all other hydrogens. Hydrogen atoms were not added to disordered groups. No significant features were present in the final difference electron density map.

Attempts to model the cocrystallized pyridine molecules gave unsatisfactory results due to extensive disorder. The use of rigid groups or fixed interatomic distances led to several large residual peaks. The data were corrected for the disordered pyridine molecules using Platon/SQUEEZE. This gave a calculated potential solvent area of 1151.3 $Å^3$ (17.3% total volume) containing 319 electrons, which is consistent with ca. 7.6 molecules of pyridine in the unit cell. The value of R1 (I>2σI) improved significantly (from 0.0702 to 0.0554) after the correction, and refinement of the model gave acceptable convergence. No significant features were present in the final difference electron density map.