Groups 5 and 6 Terminal Hydrazido(2-) Complexes: N_β Substituent Effects on LMCT Energies and Metal Formal Oxidation States

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Supporting Information

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General Considerations and Instrumentation. All air- and moisture-sensitive compounds were manipulated using standard high vacuum and Schlenk techniques or manipulated in a glovebox under a nitrogen atmosphere. Solvents for air- and moisture-sensitive reactions were dried over sodium benzophenone ketyl and stored over titanocene where compatible or dried by the method of Grubbs. Benzene-d_6 was purchased from Cambridge Isotopes and dried over sodium benzophenone ketyl. CD_2Cl_2 was degassed, distilled from CaH_2 and run through a plug of activated alumina prior to use. Liquid 1,1-disubstituted hydrazines were degassed and passed through a plug of activated alumina prior to use. ^1H and ^{13}C spectra were recorded on Varian Mercury 300 or Varian INOVA 500 spectrometers and chemical shifts are reported with respect to residual protio-solvent impurity for ^1H (*s*, 7.16 ppm for C_6D_5H; *t*, 5.32 ppm for $CDHCl_2$) and solvent carbons for ^{13}C (*t*, 128.39 for C_6H_6; *p*, 53.84 for CD_2Cl_2).

Resonance Raman Spectroscopy. The resonance Raman samples were prepared by loading solutions into capillaries in an inert atmosphere glovebox and then flame sealing the capillaries. Excitation was performed at 514 nm using an argon ion laser operating at 10 mw at the sample. A lens collected the light that scattered at 90° and focused it through a low-pass filter and into the entrance slit of a SPEX 750M monochromator. The dispersed light was detected by a LN/CCD array (5 cm^{-1} resolution), and the spectra recorded using Winspec (Princeton Instruments) software. Conversion from pixels to wavenumbers was done by obtaining the spectrum of cyclohexane and deriving the linear plot of pixels versus wavenumber for known vibrations. All spectra

were recorded in $C_2H_4Cl_2$, and in some instances, solvent subtraction or baseline correction was performed.

X-ray Crystal Data: General Procedure. Crystals were removed quickly from a scintillation vial to a microscope slide coated with Paratone N oil. Samples were selected and mounted on a glass fiber with Paratone N oil. Data collection was carried out on a Bruker KAPPA APEX II diffractometer with a 0.71073 Å MoK唸唸source. The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. Details regarding refined data and cell parameters are available in Table x and the supporting information.

General Diarylhydrazine Synthesis. All of the hydrazines were synthesized from their respective diarylamines *via* the following procedure: Diarylamine (0.01-0.03 mol, 1 equiv) was dissolved in 100 mL EtOH and cooled to 0 °C in an ice bath. 20 mL concentrated HCl was added, and the mixture was vigorously stirred for 5 minutes. $NaNO_2$ (1.1 equiv) in 20 mL H_2O was added dropwise to the reaction over the course of 5 minutes, which immediately yielded an off-white precipitate of the nitrosamine. The reaction was stirred at 0 °C for 1 hour, and then the nitrosamine was collected by filtration and used without further purification.

The nitrosamine was dried *in vacuo*, then dissolved in 150 mL dry Et_2O in a glovebox. $LiAlH_4$ (1.2 equiv) dissolved in 40 mL Et_2O was then added dropwise over the course of 1 hour to the stirring nitrosamine solution. The reaction bubbled vigorously, indicating release of H_2. After addition was complete and bubbling had subsided, the reaction was stirred for another 2 hours. Next, the reaction was removed from the glovebox and 200 mL of benchtop Et_2O was added, followed by the careful addition of

200 mL of a saturated sodium potassium tartrate solution. The resultant mixture was then extracted 3x with 200 mL Et_2O. 200 mL of HCl-acidified Et_2O was then added to the combined organics, resulting in the precipitation of the white hydrazine hydrochloride salt that was collected by filtration. The HCl salt was then deprotonated using aqueous NaOH and extracted into 500 mL Et_2O. The organics were dried using $MgSO_4$, then solvent removed *in vacuo* to yield the hydrazine as an off-white powder. Note: these hydrazines are somewhat air-sensitive and turn red/purple upon prolonged air exposure. They should be stored under an inert atmosphere.

N-aminocarbazole. Yielded 2.0 g (0.0108 mol, 28.6% yield) of the hydrazine, starting from 6.326 g (0.038 mol) carbazole. ^{1}H NMR (500 MHz, CD_2Cl_2) δ, ppm: 4.67 (*s*, 2H, N*H*$_2$), 7.24 (*t*, 2H, aryl), 7.49 (*t*, 2H, aryl), 7.57 (*d*, 2H, aryl), 8.07 (*d*, 2H, aryl). ^{13}C NMR (125 MHz, CD_2Cl_2) δ, ppm: 119.0, 119.5, 119.9, 120.1, 120.7, 141.4 (aryl).

(*p*-Cl-C$_6$H$_4$)$_2$NNH$_2$. Yielded 3.51 g (0.0139 mol, 54.2% yield) of the hydrazine, starting from 6.084 g (0.0256 mol) (*p*-Cl-Ph)$_2$NH. ^{1}H NMR (500 MHz, CD_2Cl_2) δ, ppm: 4.17 (*s*, 2H, N*H*$_2$), 7.15 (*m*, 4H, aryl), 7.24 (*m*, 4H, aryl). ^{13}C NMR (125 MHz, CD_2Cl_2) δ, ppm: 120.7, 121.3, 127.1, 129.1, 129.6, 147.8 (aryl).

(*p*-Br-C$_6$H$_4$)$_2$NNH$_2$. Yielded 5.27 g (0.0163 mol, 44% yield) of the hydrazine, starting from 12.111 g (0.037 mol) (*p*-Br-Ph)$_2$NH. ^{1}H NMR (500 MHz, CD_2Cl_2) δ, ppm: 4.17 (*s*, 2H, N*H*$_2$), 7.10 (*m*, 4H, aryl), 7.38 (*m*, 4H, aryl). ^{13}C NMR (125 MHz, CD_2Cl_2) δ, ppm: 114.5, 121.1, 121.7, 132.0, 132.5, 148.1 (aryl).

(*p*-CH$_3$-C$_6$H$_4$)$_2$NNH$_2$. Yielded 3.27 g (0.0154 mol, 52% yield) of the hydrazine, starting from 5.84 g (0.0296 mol) (*p*-CH$_3$-Ph)$_2$NH. ^{1}H NMR (500 MHz, CD_2Cl_2) δ, ppm:

2.33 (*s*, 6H, C*H*$_3$), 4.10 (*s*, 2H, N*H*$_2$), 7.10 (*m*, 8H, aryl). ^{13}C NMR (125 MHz, CD_2Cl_2) δ, ppm: 20.8 (*C*H$_3$), 119.5, 120.1, 129.6, 130.1, 131.6, 147.9 (aryl).

(*p*-CH$_3$O-C$_6$H$_4$)$_2$NNH$_2$. Yielded 1.20 g (0.0049 mol, 51.7% yield) of the hydrazine, starting from 2.176 g (0.0095 mol) (*p*-CH$_3$O-Ph)$_2$NH. ^{1}H NMR (500 MHz, CD_2Cl_2) δ, ppm: 3.77 (s, 6H, OC*H*$_3$), 4.05 (br s, 2H, N*H*$_2$), 6.82 (m, 4H, aryl), 7.06 (m, 4H, aryl). ^{13}C NMR (125 MHz, CD_2Cl_2) δ, ppm: 55.4 (O*C*H$_3$), 114.4, 121.3, 144.4, 155.0 (aryl).

General Synthesis of (dme)MCl$_3$(NNR$_2$) (M = Ta, Nb). $NbCl_5$ (1 g, 3.7 mmol, 1 equiv) and $ZnCl_2$ (1.009 g, 7.4 mmol, 2 equiv) were added in 15mL CH_2Cl_2 in an inert atmosphere glovebox. The suspension was stirred vigorously as 1 mL dimethoxyethane was slowly added, then left to stir for an additional hour. Next, the appropriate 1,1-disubstituted hydrazine (3.7 mmol, 1 equiv) and pyridine (600 µL, 585 mg, 7.4 mmol, 2 equiv) in 1 mL CH_2Cl_2 was added dropwise to the suspension of Nb and Zn over the course of 10 minutes. An immediate color change to green was observed. The reactions were left to stir overnight, yielding green solutions with white precipitate ($ZnCl_3$pyH). The solutions were filtered and CH_2Cl_2 removed *in vacuo*. The product was then extracted into 60 mL C_6H_6 and filtered again to remove residual salts. 100 mL pentane was added to the C_6H_6 solution and stirred vigorously, resulting in the hydrazide precipitating out as green microcrystals which were isolated *via* filtration and washed with 20 mL pentane. In some cases, brown or purple material oiled out or crystallized out upon addition of pentane to the benzene solutions prior to the product precipitating out. In these cases, the solutions were decanted and the supernatant cooled to -30 °C, yielding the desired product as green crystals. X-ray quality crystals were obtained from slow diffusion of pentane into a saturated solution of the product in $C_2H_4Cl_2$, or by

cooling the pentane/benzene supernatant to 30 °C. An identical procedure was utilized for (dme)$TaCl_3(NNR_2)$, beginning with 1 g (2.8 mmol) $TaCl_5$.

(dme)$TaCl_3$(Ncarbazole). Yielded 800 mg (%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ, ppm: 4.11 (*s*, 3H, C*H*$_3$O), 4.16 (*s*, 3H, C*H*$_3$O), 4.26 (*m*, 2H, OC*H*$_2$), 4.29 (*m*, 2H, OC*H*$_2$), 7.22 (*t*, 2H, aryl), 7.55 (*t*, 2H, aryl), 8.03 (*d*, 2H, aryl), 8.22 (*d*, 2H, aryl). ^{13}C NMR (125 MHz, CD_2Cl_2) δ, ppm: 64.2 (O*C*H$_2$), 71.0 (O*C*H$_2$), 72.5 (O*C*H$_3$), 76.5 (O*C*H$_3$), 111.6, 120.1, 120.3, 112.3, 126.8, 139.5 (aryl). Calcd for $C_{16}H_{18}Cl_3N_2O_2Ta$ C 34.46 H 2.53 N 5.02; Found C 39.39, H 3.62, N 5.09%.

(dme)$TaCl_3$(NN(*p*-Cl-Ph)$_2$). Yielded 1.41 g (80%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ, ppm: 3.97 (*s*, 3H, C*H*$_3$O), 4.04 (*s*, 3H, C*H*$_3$O), 4.14 (*m*, 2H, OC*H*$_2$), 4.17 (*m*, 2H, OC*H*$_2$), 7.37 (*m*, 4H, aryl), 7.41 (*m*, 4H, aryl). ^{13}C NMR (125 MHz, CD_2Cl_2) δ, ppm: 63.8 (O*C*H$_2$), 70.7 (O*C*H$_2$), 72.3 (O*C*H$_3$), 76.4 (O*C*H$_3$), 121.5, 121.7, 122.1, 122.3, 128.9, 129.1, 129.5, 129.8, 130.0, 141.6 (aryl).

(dme)$TaCl_3$(NN(*p*-Br-Ph)$_2$). Yielded 1.10 g (54.8%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ, ppm: 3.97 (*s*, 3H, C*H*$_3$O), 4.04 (*s*, 3H, C*H*$_3$O), 4.14 (*m*, 2H, OC*H*$_2$), 4.17 (*m*, 2H, OC*H*$_2$), 7.36 (*m*, 4H, aryl), 7.51 (*m*, 4H, aryl). ^{13}C NMR (125 MHz, CD_2Cl_2) δ, ppm: 63.8 (O*C*H$_2$), 70.9 (O*C*H$_2$), 72.3 (O*C*H$_3$), 76.4 (O*C*H$_3$), 117.7, 121.8, 122.0, 122.5, 122.7, 131.9, 132.1, 132.4, 132.7, 142.0 (aryl). Calcd for $C_{16}H_{18}Br_2Cl_3N_2O_2Ta$: C 26.79, H 2.53, N 3.90; Found C 27.32, H 2.55, N 3.79%.

(dme)$TaCl_3$(NNPh_2). Yielded 1.32 g (84.3%). Spectral data same as previously reported in reference 10.

(dme)$NbCl_3$(Ncarbazole). Yielded 410 mg (23.6%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ, ppm: 4.00 (*s*, 3H, C*H*$_3$O), 4.10 (*s*, 3H, C*H*$_3$O), 4.23 (*s*, 4H, OC*H*$_2$), 7.31 (*t*, 2H, aryl), 7.56 (*t*, 2H, aryl), 7.99 (*d*, 2H, aryl), 8.36 (*d*, 2H, aryl). ^{13}C NMR (125 MHz, CD_2Cl_2) δ, ppm: 63.2 (O*C*H$_2$), 69.4 (O*C*H$_2$), 71.9 (O*C*H$_3$), 75.7 (O*C*H$_3$), 111.8, 112.0, 120.0, 122.6, 127.0, 139.1 (aryl). Calcd for $C_{16}H_{18}Cl_3N_2NbO_2$: C 40.92, H 3.86, N 5.97; Found: C 40.81, H 3.83, N 6.05%.

(dme)$NbCl_3$(NN(*p*-Cl-Ph)$_2$). Yielded 850 mg (42.5%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ, ppm: 3.83 (*s*, 3H, C*H*$_3$O), 3.96 (*s*, 3H, C*H*$_3$O), 4.10 (*s*, 4H, OC*H*$_2$), 7.40 (*m*, 4H, aryl), 7.47 (*m*, 4H, aryl). ^{13}C NMR (125 MHz, CD_2Cl_2) δ, ppm: 62.8 (O*C*H$_2$), 69.2 (O*C*H$_2$), 71.6 (O*C*H$_3$), 75.6 (O*C*H$_3$), 121.1, 121.5, 122.0, 128.9, 129.2, 129.8, 130.8, 140.0 (aryl). Calcd for $C_{16}H_{18}Cl_5N_2NbO_2$: C 35.55, H 3.36, N 5.18; Found C 35.81, H 3.59, N 5.14%.

(dme)$NbCl_3$(NN(*p*-Br-Ph)$_2$). Yielded 525 mg (22.5%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ, ppm: 3.83 (*s*, 3H, C*H*$_3$O), 3.96 (*s*, 3H, C*H*$_3$O), 4.11 (*s*, 4H, OC*H*$_2$), 7.41 (*m*, 4H, aryl), 7.55 (*m*, 4H, aryl). ^{13}C NMR (125 MHz, CD_2Cl_2) δ, ppm: 62.8 (O*C*H$_2$), 69.2 (O*C*H$_2$), 71.6 (O*C*H$_3$), 75.5 (O*C*H$_3$), 118.5, 121.5, 121.8, 122.3, 131.9, 132.4, 140.4 (aryl). Calcd for $C_{16}H_{18}Br_2Cl_3N_2NbO_2$: C 30.53, H 2.88, N 4.45; Found C 31.76, H 2.88, N 4.54%.

(dme)$NbCl_3$(NNPh$_2$). Yielded 1 g (57.3%). Spectral data same as previously reported in reference 10.

(dme)$NbCl_3$(NN(*p*-CH_3-Ph)$_2$). Yielded 100 mg (5.4%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ, ppm: 2.39 (*s*, 6H, C_6H_4C*H*$_3$), 3.85 (*s*, 3H, C*H*$_3$O), 3.93 (*s*, 3H, C*H*$_3$O), 4.08 (*s*, 4H, OC*H*$_2$), 7.22 (*m*, 4H, aryl), 7.35 (*m*, 4H, aryl). ^{13}C NMR (125 MHz, CD_2Cl_2) δ, ppm: 20.6 (*C*H$_3$), 62.6 (O*C*H$_2$), 69.1 (O*C*H$_2$), 71.5 (O*C*H$_3$), 75.4 (O*C*H$_3$), 120.0, 129.3, 135.3, 139.2 (aryl). Calcd for $C_{18}H_{24}Cl_3N_2NbO_2$: C 43.27, H 4.84, N 5.61; Found C 43.59, H 4.76, N 5.68%.

(dme)$NbCl_3$(NN(*p*-CH_3O-Ph)$_2$). Yielded 120 mg (6.1%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ, ppm: 3.81 (*s*, 6H, $C_6H_4OCH_3$), 3.85 (*s*, 3H, CH_3O), 3.92 (*s*, 3H, CH_3O), 4.08 (*m*, 4H, OCH_2), 6.95 (*m*, 4H, aryl), 7.37 (*m*, 4H, aryl).

(dme)$NbCl_3$(NNPhMe). Yielded 111 mg (7.3%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ, ppm: 3.88 (*s*, 3H, NCH_3), 3.95 (*s*, 3H, CH_3O), 4.03 (*s*, 3H, CH_3O), 4.11 (*m*, 2H, OCH_2), 4.17 (*m*, 2H, OCH_2), 6.92 (*t*, 1H, aryl), 7.30 (*d*, 2H, aryl), 7.37 (*t*, 2H, aryl). ^{13}C NMR (125 MHz, CD_2Cl_2) δ, ppm: 62.5 (OCH_2), 69.2 (OCH_2), 71.5 (OCH_3), 75.5 (OCH_3), 112.4, 122.7, 128.4, 143.8 (aryl). Calcd for $C_{11}H_{18}Cl_3N_2NbO_2$: C 32.26, H 4.43, N 6.84; Found C 32.07, H 4.36, N 6.72%.

(dme)$NbCl_3$(NNMe_2). Yielded 732 mg (56.9%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ, ppm: 3.14 (*s*, 6H, $N(CH_3)_2$), 3.86 (*s*, 3H, CH_3O), 4.03 (*m*, 2H, OCH_2), 4.10 (*m*, 2H, OCH_2), 4.10 (*s*, 3H, CH_3O). ^{13}C NMR (125 MHz, CD_2Cl_2) δ, ppm: 43.6 ($N(CH_3)_2$), 62.1 (OCH_2), 69.1 (OCH_2), 71.3 (OCH_3), 75.4 (OCH_3).

(dme)$NbCl_3$(Npiperidyl). Yielded 150 mg (10.5%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ, ppm: 1.47 (*m*, 2H, $N(CH_2)_4CH_2$) 1.66 (*m*, 4H, $N(CH_2)_2(CH_2)_2CH_2$), 3.14 (*s*, 6H, $N(CH_3)_2$), 3.49 (*m*, 4H, $N(CH_2)_2(CH_2)_3$), 3.86 (*s*, 3H, CH_3O), 4.02 (*m*, 2H, OCH_2), 4.09 (*m*, 2H, OCH_2), 4.09 (*s*, 3H, CH_3O). ^{13}C NMR (125 MHz, CD_2Cl_2) δ, ppm: 23.8 (CH_2); 25.3 (CH_2); 54.6 (CH_2); 62.5 (OCH_2), 69.2 (OCH_2), 71.6 (OCH_3), 75.7 (OCH_3). Calcd for $C_9H_{20}Cl_3N_2NbO_2$: C 27.89, H 5.20, N 7.23; Found C 27.79, H 4.99, N 7.22%.

General Synthesis of (MeCN)WCl_4(NNR_2). A modified literature procedure was used. WCl_6 (1 g, 2.52 mmol, 1 equiv) was slurried in 15 mL CH_2Cl_2 in an inert atmosphere glovebox. The appropriate 1,1-disubstituted hydrazine (2.52 mmol, 1 equiv) dissolved in 2 mL CH_2Cl_2 was added dropwise to the slurried WCl_6 over the course

of 10 minutes. The reaction was left to stir for 1 hour, then 1 mL MeCN was added. The reaction was stirred for 1 hour and then filtered. The dark filtrate was then added to 150 mL of vigorously stirred pentane, which resulted in the precipitation of the desired product as an orange or purple microcrystalline material. The product was collected *via* filtration and washed with 20 mL pentane.

$(CH_3CN)WCl_4$(Ncarbazole). Yielded (%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ, ppm: 2.63 (*s,* 3H, C*H*$_3$CN), 7.07 (*t*, 2H, aryl), 7.68 (*t*, 2H, aryl), 7.92 (*d*, 2H, aryl), 8.10 (*d*, 2H, aryl). ^{13}C NMR (125 MHz, CD_2Cl_2) δ, ppm: 4.4 (*C*H$_3$CN), 121.6 (CH$_3$*C*N), 115.8, 119.8, 123.8, 126.5, 129.0, 134.2 (aryl). Calcd for $C_{14}H_{11}Cl_4N_3W$: C 30.75, H 2.03, N 7.68; Found C 28.98, H 2.29, N 7.27%.

$(CH_3CN)WCl_4$(NN(*p*–Cl–Ph)$_2$). Yielded 1.15 g (73.9%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ, ppm: 2.56 (*s,* 3H, C*H*$_3$CN), 7.21 (*m*, 4H, aryl), 7.67 (*m*, 4H, aryl). ^{13}C NMR (125 MHz, CD_2Cl_2) δ, ppm: 4.4 (*C*H$_3$CN), 121.3 (CH$_3$*C*N), 126.2, 126.7, 128.8, 129.0, 129.1, 129.4, 129.5, 131.5, 136.9 (aryl.)

$(CH_3CN)WCl_4$(NN(*p*–Br–Ph)$_2$). Yielded 1.40 g (79.2%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ, ppm: 2.55 (*s,* 3H, C*H*$_3$CN), 7.15 (*m*, 4H, aryl), 7.82 (*m*, 4H, aryl). ^{13}C NMR (125 MHz, CD_2Cl_2) δ, ppm: 4.4 (*C*H$_3$CN), 120.9 (CH$_3$*C*N), 124.5, 125.6, 126.0, 126.5, 131.5, 131.7, 131.8, 131.9, 132.1 (aryl.)

X-Ray Crystallography Data

Table S1. Bond distances and sum of angles about N_β in (dme)$MCl_3(NNR_2)$ and (MeCN)$WCl_4(NNR_2)$.

M	R_2	M–N (Å)	N–N (Å)	Σ (°$_{N\beta}$)
Ta	$C_{12}H_8$ (**1a**)	1.7605(1)	1.3609(1)	359.0
	(*p*–BrPh)$_2$ (**1c**)	1.760	1.3608	358.7
	Ph_2 (**1d**)[a]	1.773(1)	1.347(1)	359.7
	(*p*–CH_3Ph)$_2$ (**1e**)	1.7739(3)	1.3400(2)	358.8
Nb	$C_{12}H_8$ (**2a**)	1.7742(1)	1.3282(1)	359.9
	(*p*–ClPh)$_2$ (**2b**)	1.7661(1)	1.3335(1)	359.1
	(*p*–BrPh)$_2$ (**2c**)	1.7719(1)	1.3374(1)	360.0
	Ph_2 (**2d**)[a]	1.7654(1)	1.3447(1)	359.9
	(*p*–CH_3Ph)$_2$ (**2e**)	1.7684(1)	1.3305(1)	359.6
	(*p*–CH_3OPh)$_2$ (**2f**)	1.7701(1)	1.3362(1)	359.5
	(CH_3)(Ph) (**2g**)	1.7726(1)	1.3242(1)	360.0
	(CH_3)$_2$ (**2h**)	1.7601(1)	1.3508(1)	342.1
	C_5H_{10} (**2i**)	1.7597(1)	1.3392(1)	341.1
W	Ph_2 (**3d**)[b]	1.742(4)	1.312(5)	359.3
	(CH_3)$_2$ (**3h**)[b]	1.769(5)	1.271(8)	360.0
	C_5H_{10} (**3i**)	1.7633(1)	1.2556(1)	359.8

[a]Taken from ref. 10. [b]Taken from ref. 12. [c]Taken from ref. 16.

Table S2. Crystal and refinement data for complexes **1a**, **1c**, and **1e**.

	1a	**1c**	**1e**
CCDC Number	855853	856712	854441
Empirical formula	$C_{16}H_{18}N_2O_2Cl_3Ta \cdot C_6H_6$	$C_{16}H_{16}N_2O_2Br_2Cl_3Ta$	$C_{18}H_{24}Cl_3N_2O_2Ta$
Formula weight	635.73	717.43	587.69
T (K)	100(2)	100(2)	100(2)
a, Å	10.9765(4)	7.2890(3)	7.3415(4)
b, Å	14.9892(6)	13.3859(5)	9.2663(5)
c, Å	15.2682(6)	10.9809(4)	9.2663(5)
唸, deg			78.390(3)
唸, deg	110.395(2)	90.292(1)	84.353(3)
唸, deg			84.864(2)
Volume, Å^3	2354.58(16)	1071.39(7)	1075.72(10)
Z	4	2	2
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1$	P-1
d_{calc}, g/cm^3	1.793	2.218	1.814
唸 range, deg	1.97 to 43.56	1.85 to 30.53	2.25 to 51.69
μ, mm^{-1}	5.030	11.000	5.496
Abs. Correction	Semi-Empirical	Semi-Empirical	Semi-Empirical
GOF	1.892	1.455	1.218
R_1 ,[a]	R1 = 0.0253,	R1 = 0.0196,	R1 = 0.0237,
wR_2 [b] [I>2唸(I)]	*w*R2 = 0.0359	*w*R2 = 0.0380	*w*R2 = 0.0343

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table S3. Crystal and refinement data for complexes **2a**, **2b**, and **2c**.

	2a	**2b**	**2c**
CCDC Number	85445	855001	856445
Empirical formula	$C_{16}H_{18}Cl_3N_2NbO_2$	$C_{16}H_{18}N_2O_2Cl_5Nb$	$C_{16}H_{18}Br_2Cl_3N_2NbO_2$
Formula weight	469.58	540.48	629.40
T (K)	100(2)	100(2)	100(2)
a, Å	19.4748(9)	7.3791(4)	8.8532(4)
b, Å	9.6654(4)	8.9250(4)	26.6360(13)
c, Å	19.3262(9)	16.3801(8)	9.4480(5)
喻, deg		80.331(2)	
喻, deg	93.727(2)	84.651(2)	99.838(2)
喻, deg		85.152(2)	
Volume, Å^3	3630.1(3)	1056.20(9)	2195.21(19)
Z	8	2	4
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	C 2/*c*	P–1	$P2_1/n$
d_{calc}, g/cm^3	1.718	1.699	1.904
喻 range, deg	2.10 to 55.67	2.32 to 40.82	2.32 to 45.45
μ, mm^{-1}	1.116	1.216	4.567
Abs. Correction	None	None	None
GOF	2.165	2.169	1.445
R_1 ,[a]	R1 = 0.0263,	R1 = 0.0203,	R1 = 0.0247,
wR_2 [b] [I>2喻(I)]	*w*R2 = 0.0445	*w*R2 = 0.0515	*w*R2 = 0.0401

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table S4. Crystal and refinement data for complexes **2e**, **2f**, and **2g**.

	2e	**2f**	**2g**
CCDC Number	855000	856713	855003
Empirical formula	$C_{18}H_{24}N_2O_2Cl_3Nb$	$C_{18}H_{24}N_2O_4Cl_3Nb \cdot 0.5(C_7H_8)$	$C_{11}H_{18}N_2O_2Cl_3Nb$
Formula weight	499.65	577.72	409.53
T (K)	100(2)	100(2)	100(2)
a, Å	7.3620(4)	7.4401(3)	7.6003(4)
b, Å	9.2470(5)	10.5793(5)	10.5217(6)
c, Å	16.2248(10)	16.3555(7)	11.2752(6)
唸, deg	78.177(3)	97.7650(10)°	64.736(2)
唸, deg	85.220(3)	95.120(2)°	79.530(2)
唸, deg	84.498(3)	99.874(2)°	83.340(2)
Volume, Å^3	1073.81(11)	1248.30(9)	801.09(8)
Z	2	2	2
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P–1	P–1	P–1
d_{calc}, g/cm^3	1.545	1.537	1.698
唸 range, deg	2.26 to 44.88	1.26 to 30.57	2.02 to 51.72
μ, mm^{-1}	0.948	0.830	1.250
Abs. Correction	None	Semi Empirical	None
GOF	2.163	2.445	2.009
R_1 ,[a]	R1 = 0.0237,	R1 = 0.0332,	R1 = 0.0223,
wR_2 [b] [I>2唸(I)]	*w*R2 = 0.0556	*w*R2 = 0.0624	*w*R2 = 0.0476

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table S5. Crystal and refinement data for complexes **2h**, **2i**, and **3i**.

	2h	**2i**	**3i**
CCDC Number	855020	855260	855852
Empirical formula	$C_6H_{16}N_2O_2Cl_3Nb$	$C_9H_{20}N_2O_2Cl_3Nb$	$C_7H_{13}N_3Cl_4W$
Formula weight	347.47	387.53	464.85
T (K)	100(2)	100(2)	100(2)
a, Å	20.6913(14)	6.8865(3)	9.6582(4)
b, Å	12.5611(8)	12.1853(5)	14.7762(7)
c, Å	15.4117(10)	18.5285(8)	9.7818(4)
喻, deg			
喻, deg	90.294(4)		92.958(2)
喻, deg			
Volume, Å^3	4005.5(5)	1554.80(11)	1394.12(10)
Z	12	4	4
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$P2_12_12_1$	$P2_1/n$
d_{calc}, g/cm^3	1.729	1.656	2.215
喻 range, deg	1.90 to 44.67	2.00 to 47.65	2.50 to 53.16
μ, mm^{-1}	1.482	1.282	9.026
Abs. Correction	None	None	Semi Empirical
GOF	1.516	1.310	1.462
R_1 ,[a]	R1 = 0.0287,	R1 = 0.0313,	R1 = 0.0210,
wR_2 [b] [I>2喻(I)]	*w*R2 = 0.0408	*w*R2 = 0.0417	*w*R2 = 0.0323

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.