Electronic Supplementary Material (ESI) for Dalton Transactions

SUPPORTING INFORMATION

Synthesis and Investigation of the Metal-Metal Interactions in Early/Late Heterobimetallic Complexes Linking Group 5 Imido Fragments to Co(I).

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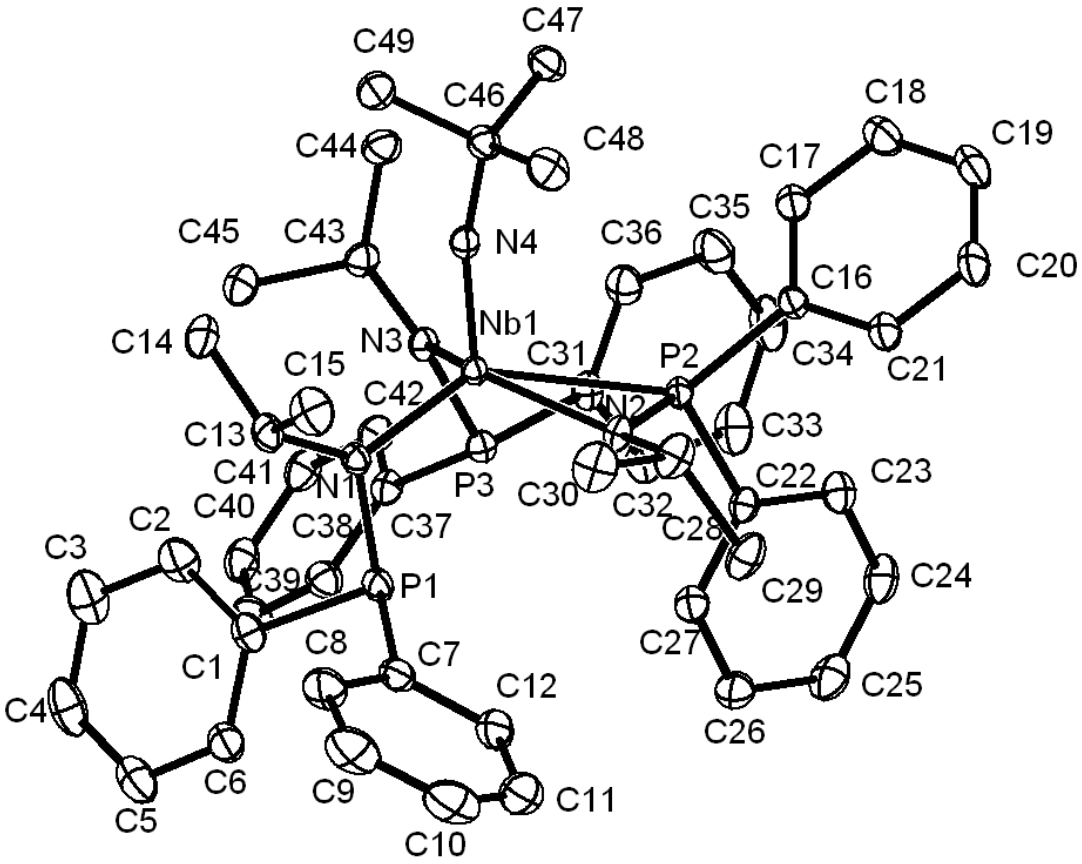
Figure S1. Fully-labeled ellipsoid representation of $\mathbf{1}^{Nb}$.



X-Ray data collection, solution, and refinement for 1^{Nb}. All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated MoKα radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software.[1] Preliminary cell constants were obtained from three sets of 12 frames. Data collection was carried out at 120 K, using a frame time of 10 sec and a detector distance of 60 mm. The optimized strategy used for data collection consisted of six phi and four omega scan sets, with 0.5° steps in phi or omega; completeness was 99.4%. A total of 3284 frames were collected. Final cell constants were obtained from the xyz centroids of 9886 reflections after integration.

From the systematic absences, the observed metric constants and intensity statistics, space group $P\bar{1}$ was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved using SuperFlip,[2] and refined (full-matrix-least squares) using the Oxford University *Crystals for Windows* program.[3] All non-hydrogen atoms were refined using anisotropic displacement parameters. After location of H atoms on electron-density difference maps, the H atoms were initially refined with soft restraints on the bond lengths and angles to regularise their geometry (C---H in the range 0.93--0.98 Å and U_{iso} (H) in the range 1.2-1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.[4] The final least-

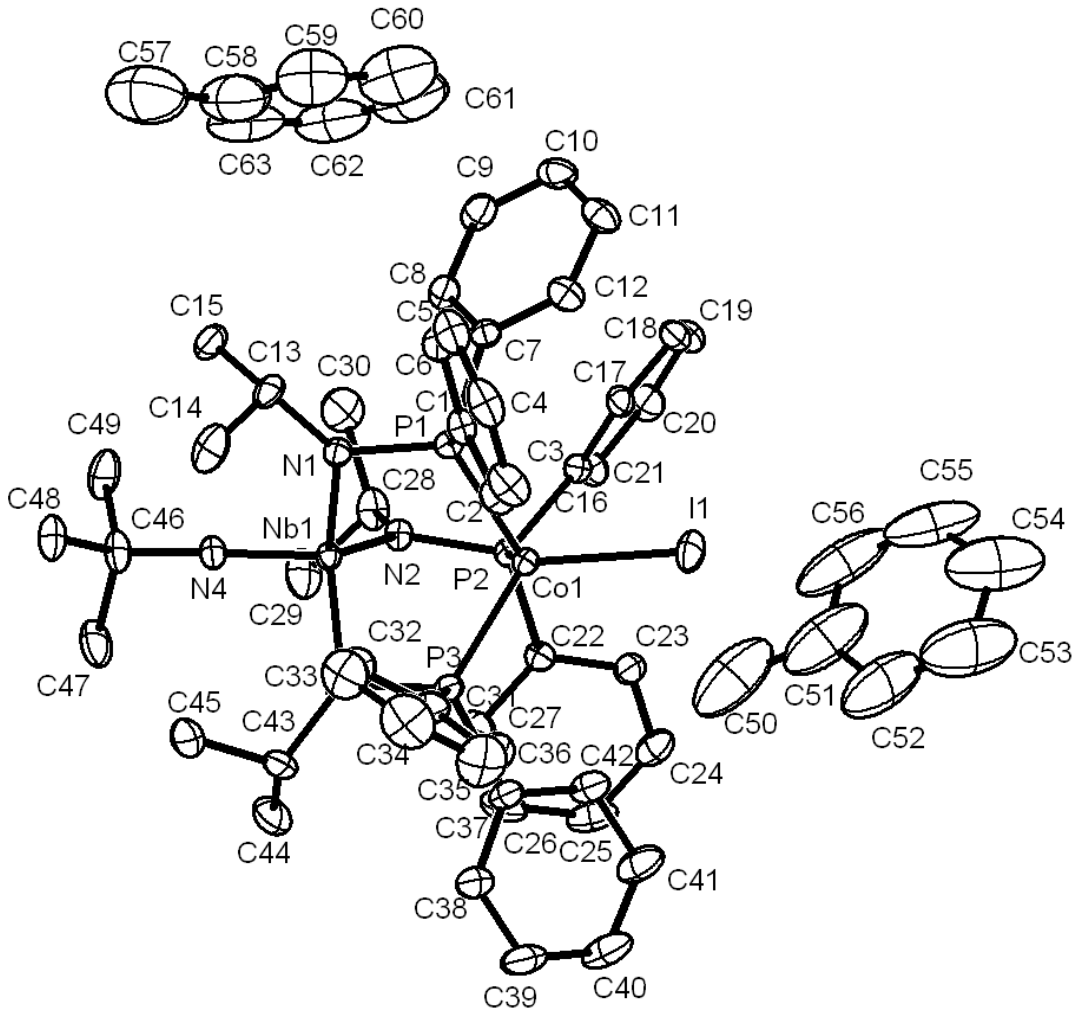
[1] Apex2, Version 2 User Manual, M86-E01078, Bruker Analytical X-ray Systems, Madison, WI, June 2006.
[2] Palatinus, L.; Chapuis, G.; *J. Appl. Cryst*. **2007**, 40, 786.

[3] Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J. *J. Appl. Cryst.* **2003**, *36*, 1487; Prout, C.K;. Pearce, L.J. CAMERON, Chemical Crystallography Laboratory, Oxford, UK, 1996.

squares refinement converged to R_1 = 0.0317 ($I > 2\sigma(I)$, 10666 data) and wR_2 = 0.0733 (F^2, 13461 data, 514 parameters). The final CIF is available as supporting material.

[4] Cooper, R. I.; Thompson, A. L.; Watkin, D. J. *J. Appl. Cryst.* **2010**, *43*, 1100–1107.

Figure S2. Fully-labeled ellipsoid representation of **2**^{Nb}•2toluene**.**

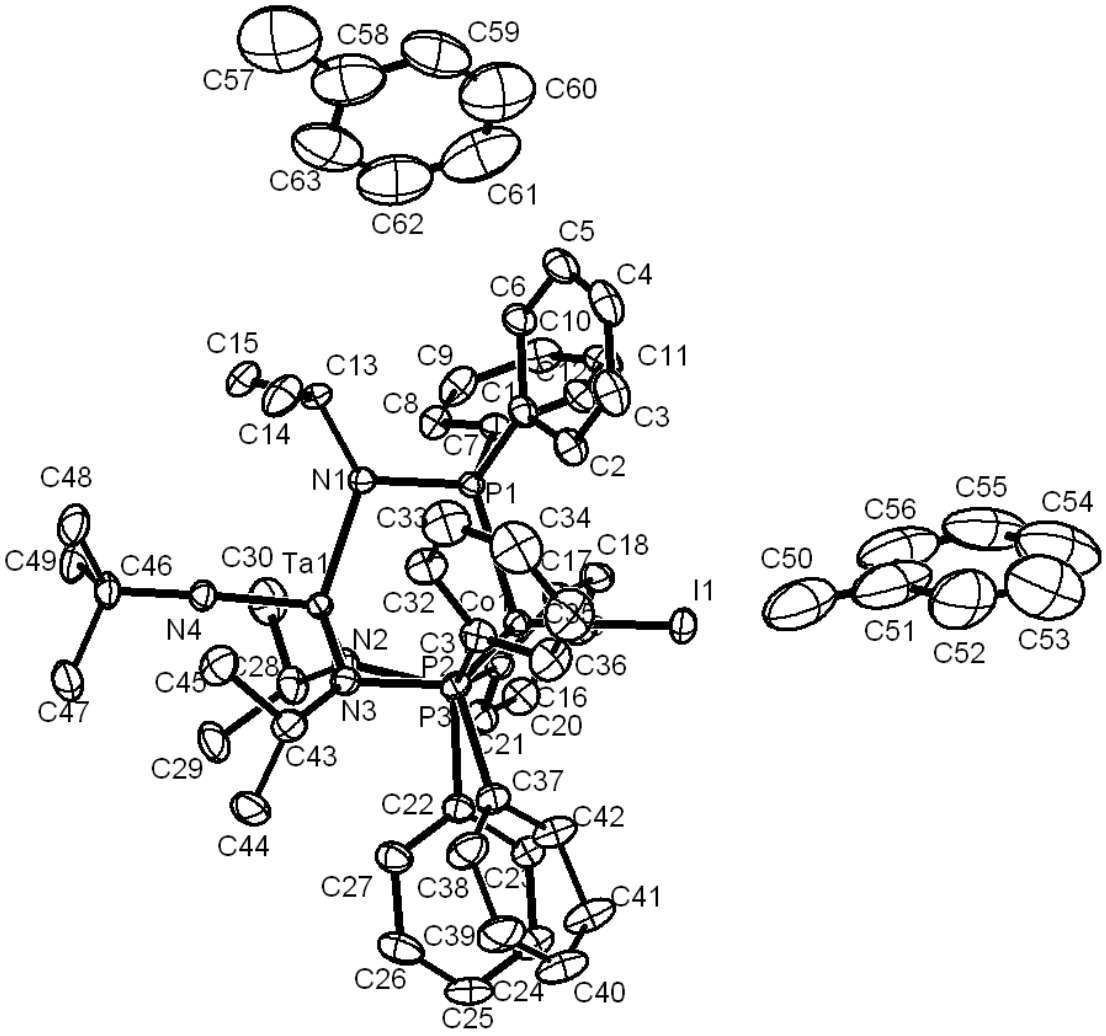


X-Ray data collection, solution, and refinement for 2^{Nb}. All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated MoKα radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software.[1] Preliminary cell constants were obtained from three sets of 12 frames. Data collection carried out at 120K, using a frame time of 10 sec and a detector distance of 60 mm. The optimized strategy used for data collection consisted of four phi and two omega scan sets, with 0.5° steps in phi or omega; completeness was 99.5%. A total of 1865 frames were collected. Final cell constants were obtained from the xyz centroids of 9824 reflections after integration.

From the systematic absences and the observed metric constants and intensity statistics, space group $P2_1/c$ was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved using *SuperFlip* and subsequent electron-density difference syntheses.[2] Refinement (full-matrix-least squares) was carried out using the Oxford University *Crystals for Windows* program.[3] All non-hydrogen atoms were refined using anisotropic displacement parameters. After location of H atoms on electron-density difference maps, the H atoms were initially refined with soft restraints on the bond lengths and angles to regularise their geometry (C---H in the range 0.93--0.98 Å and U_{iso} (H) in the range 1.2-1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.[4] During the structure solution, electron density difference maps revealed that there were considerable disordered solvent molecules; the asymmetric unit contains two disordered toluene molecules. The toluene solvate molecules were refined with distance and thermal similarity restraints. Details of

the restraints have been included as a restraint command set in the deposited CIF file. The final least-squares refinement converged to $R_1 = 0.0398$ ($I > 2\sigma(I)$, 13273 data) and $wR_2 = 0.0992$ (F^2, 17598 data, 658 parameters). The final CIF is available as supporting material.

Figure S3. Fully-labeled ellipsoid representation of **2**^{Ta}•2toluene**.**

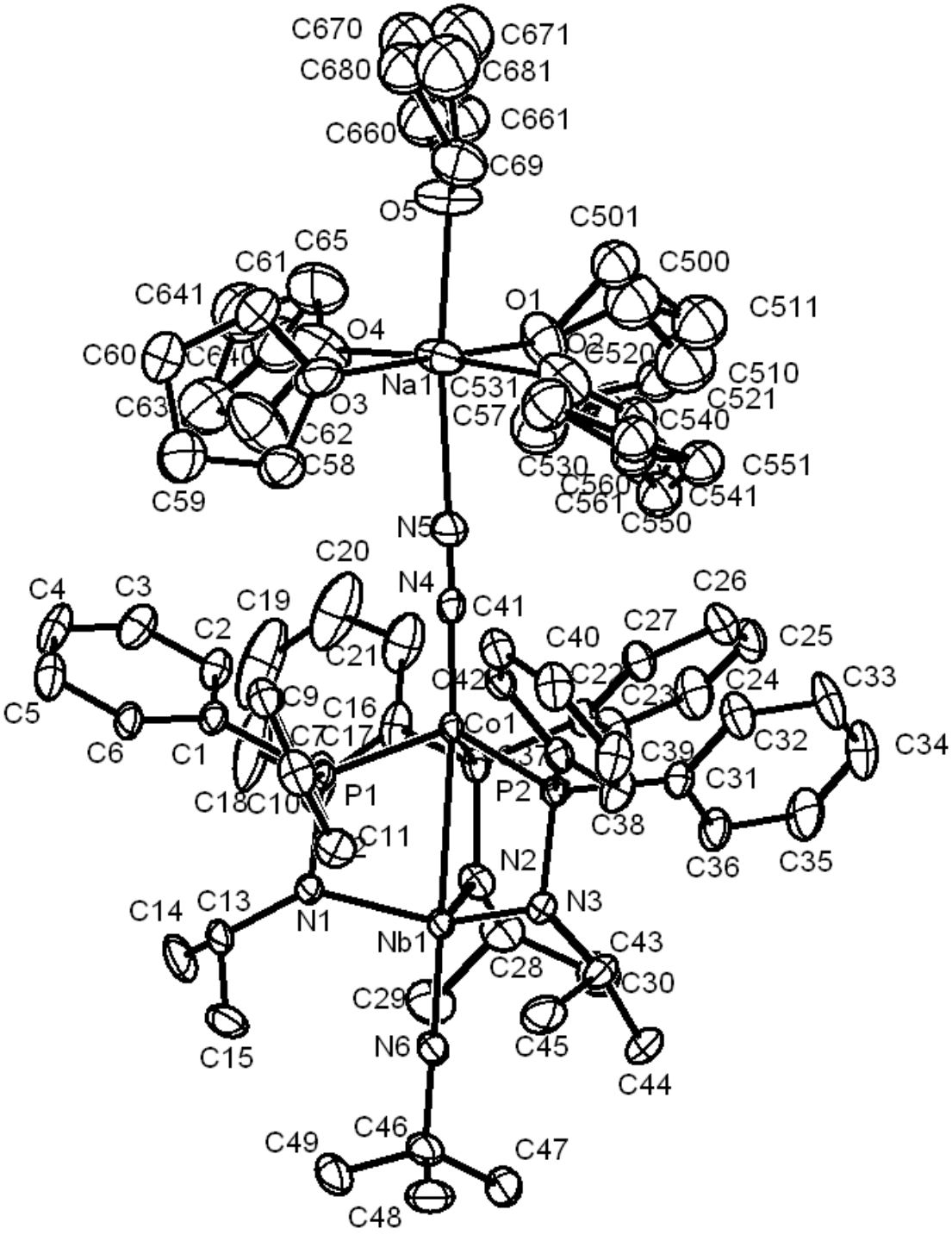


X-Ray data collection, solution, and refinement for 2^{Ta}•2toluene**.** All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated MoKα radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software.[1] Preliminary cell constants were obtained from three sets of 12 frames. Data collection carried out at 120K, using a frame time of 10 sec and a detector distance of 60 mm. The optimized strategy used for data collection consisted of three phi and one omega scan sets, with 0.5° steps in phi or omega. Unfortunately, the data collection terminated early owing to a non-recoverable failure of the server computer, requiring repairs that took several days. Nonetheless, a data set of good quality was obtained, with a completeness of 98.5%. A total of 1265 frames were collected. Final cell constants were obtained from the xyz centroids of 9967 reflections after integration.

From the systematic absences and the observed metric constants and intensity statistics, space group $P2_1/c$ was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved using *SuerFlip* and subsequent electron-density difference syntheses.[2] Refinement (full-matrix-least squares) was carried out using the Oxford University *Crystals for Windows* program.[3] All non-hydrogen atoms were refined using anisotropic displacement parameters. After location of H atoms on electron-density difference maps, the H atoms were initially refined with soft restraints on the bond lengths and angles to regularise their geometry (C---H in the range 0.93--0.98 Å and U_{iso} (H) in the range 1.2-1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.[4] During the structure solution, electron density difference maps revealed that there were considerable disordered solvent

molecules; the asymmetric unit contains two disordered toluene molecules. The toluene solvate molecules were refined with distance and thermal similarity restraints. Details of the restraints have been included as a restraint command set in the deposited CIF file. The final least-squares refinement converged to $R_1 = 0.0248$ ($I > 2\sigma(I)$, 14745 data) and $wR_2 = 0.0635$ (F^2, 17465 data, 658 parameters). The final CIF is available as supporting material.

Figure S4. Fully-labeled ellipsoid representation of **3**^{Nb}**.**

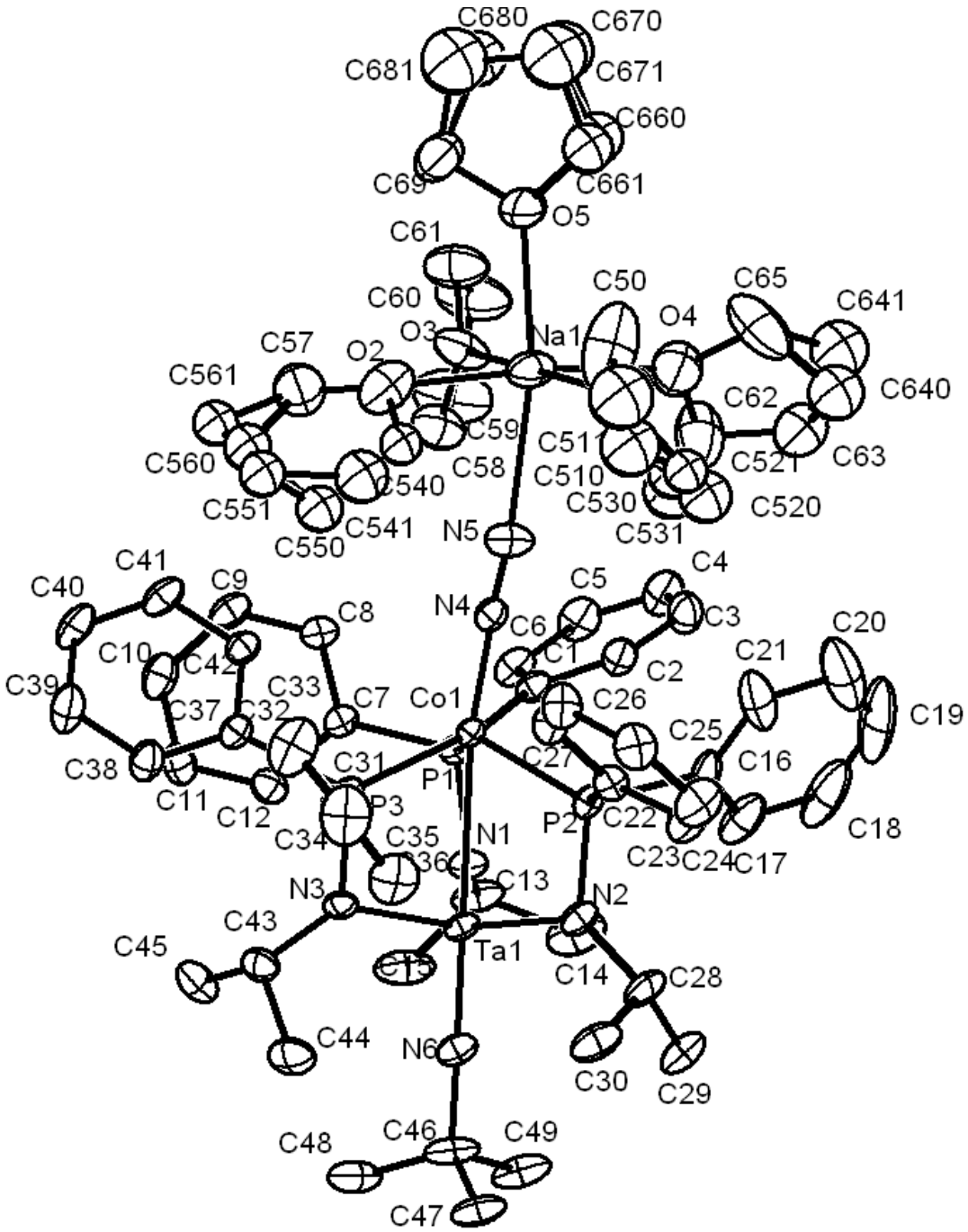


X-Ray data collection, solution, and refinement for 3^{Nb}. All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated MoKα radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software.[1] Preliminary cell constants were obtained from three sets of 12 frames. Data collection was carried out at 120K, using a frame time of 20 sec and a detector distance of 60 mm. The optimized strategy used for data collection consisted of four phi and six omega scan sets, with 0.5° steps in phi or omega; completeness was 99.5%. A total of 3248 frames were collected. Final cell constants were obtained from the xyz centroids of 8993 reflections after integration.

From the systematic absences, the observed metric constants and intensity statistics, space group *P*1 was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved using the coordinates of the isomorphous Ta analogue (**3^{Ta}**), and changing the identity of the Ta atom to Nb. The structure was refined (full-matrix-least squares) using the Oxford University *Crystals for Windows* program.[3] All ordered non-hydrogen atoms were refined using anisotropic displacement parameters. Four of the five THF molecules bonded to Na(1) were significantly disordered. The THF molecules have O atoms labeled O(1) through O(5), with molecule "O(3)" ordered. Each of the other four THF molecules was disordered, and the disorder was partially resolved in each case. Occupancies of the disordered atoms were fixed at 0.5 and the atoms were refined by using isotropic displacement parameters For the molecule containing atom O(1), the disordered pairs were: C(500)/C(501), C(510)/C(511), C(520)/C(521) and C(530)/C(531); for the molecule

containing O(2): C(540)/C(541), C(550)/C(551) and C(560)/C(561); for the molecule containing O(4): C(640)/C(641); and for the molecule containing O(5), C(660)/C(661), C(670)/C(671) and C(680)/C(681). The absolute configuration was established by Flack parameter refinement (-0.02(1)). After location of H atoms on electron-density difference maps, the H atoms attached to ordered atoms were initially refined with soft restraints on the bond lengths and angles to regularise their geometry (C---H in the range 0.93--0.98 Å and U_{iso} (H) in the range 1.2-1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.[4] The remaining H atoms on disordered THF carbon atoms were placed at geometric positions and refined with riding constraints. The final least-squares refinement converged to R_1 = 0.0347 ($I > 2\sigma(I)$, 12445 data) and wR_2 = 0.0883 (F^2, 13788 data, 764 parameters). The final CIF is available as supporting material; we note that the CheckCIF routine produced one alert B item, related to unresolved disorder. Accordingly, the CIF file contains a validation reply form item which explains this issue in detail.

Figure S5. Fully-labeled ellipsoid representation of **3**^{Ta}**.**



X-Ray data collection, solution, and refinement for 3^{Ta}. All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated MoKα radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software.[1] Preliminary cell constants were obtained from three sets of 12 frames. Data collection was carried out at 120K, using a frame time of 20 sec and a detector distance of 60 mm. The optimized strategy used for data collection consisted of four phi and six omega scan sets, with 0.5° steps in phi or omega; completeness was 99.3%. A total of 3020 frames were collected. Final cell constants were obtained from the xyz centroids of 9886 reflections after integration.

From the systematic absences, the observed metric constants and intensity statistics, space group *P*1 was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved using the Patterson function to obtain Ta and Co relative positions, and the remaining atoms were located on electron density difference maps. The structure was refined (full-matrix-least squares) using the Oxford University *Crystals for Windows* program.[3] All ordered non-hydrogen atoms were refined using anisotropic displacement parameters. Four of the five THF molecules bonded to Na(1) were significantly disordered. The THF molecules have O atoms labeled O(1) through O(5), with molecule "O(3)" ordered. Each of the other four THF molecules was disordered, and the disorder was partially resolved in each case. Occupancies of the disordered atoms were fixed at 0.5 and the atoms were refined by using isotropic displacement parameters For the molecule containing atom O(1), the disordered pairs were: C(510)/C(511), C(520)/C(521) and C(530)/C(531); for the

molecule containing O(2): C(540)/C(541), C(550)/C(551) and C(560)/C(561); for the molecule containing O(4): C(640)/C(641); and for the molecule containing O(5), C(660)/C(661), C(670)/C(671) and C(680)/C(681). The absolute configuration was established by Flack parameter refinement (-0.017(3)). After location of H atoms on electron-density difference maps, the H atoms attached to ordered atoms were initially refined with soft restraints on the bond lengths and angles to regularise their geometry (C---H in the range 0.93--0.98 Å and U_{iso} (H) in the range 1.2-1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.[4] The remaining H atoms on disordered THF carbon atoms were placed at geometric positions and refined with riding constraints. The final least-squares refinement converged to $R_1 = 0.0324$ ($I > 2\sigma(I)$, 18844 data) and $wR_2 = 0.0723$ (F^2, 19327 data, 765 parameters). The final CIF is available as supporting material; we note that the CheckCIF routine produced one alert B item, related to unresolved disorder. Accordingly, the CIF file contains a validation reply form item which explains this issue in detail.