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Complexes of Tricoordinate Hypervalent Pnictogens with Pentamethylcyclopentadienylruthenium‡

Anthony J. Arduengo, III,* Michael Lattman,*† Joseph C. Calabrese, and Paul J. Fagan

Central Research and Development Department, E. I. du Pont de Nemours & Company, Experimental Station, Wilmington, Delaware 19880-0328, U.S.A.

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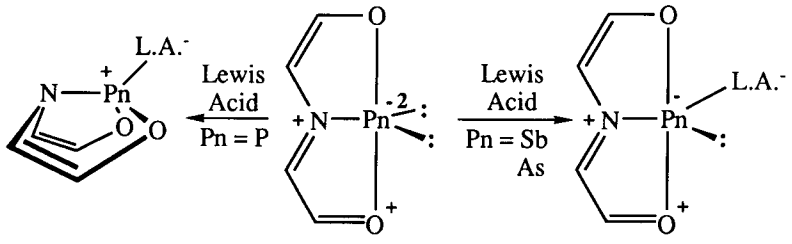
ABSTRACT

The complexes of a pentamethylcyclopentadienylruthenium moiety with hypervalent tricoordinate pnictogens are reported. A unique mode of complexation is observed for each of the different pnictogens (P, As, Sb). The phosphorus derived complex exhibits an 8-electron tetrahedral bonding environment at phosphorus. The antimony derived complex maintains a 10-electron bonding system at antimony with a pseudo-trigonalbipyramidal geometry at antimony. The arsenic-containing complex is formed with destruction of the original arsenic heterocycle and formation of a trinuclear Ru–Ru–As ring. Remarkably, the formation of the arsenic ruthenium complex can be reversed to reconstruct the original arsenic heterocycle.

INTRODUCTION

In previous reports [1–5] we have described the complexation chemistry observed between some transition metal centers and a series of novel pnictogen heterocycles (ADPnO systems) [6] containing tricoordinate hypervalent pnictogen centers (10-Pn-3) [7]. Trends from our earlier work have established two complexation modes for these ADPnO systems (Equation 1). The mode of complexation observed for the phosphorus-derived system is characterized by a folding of the ADPO ring system to provide an 8-electron phosphorus center for coordination to the transition metal center. This folding allows a tetrahedral geometry at the complexed phosphorus center. The arsenic- and antimony-derived systems follow a second mode of complexation that involves maintaining the hypervalent, 10-electron bonding environment at the pnictogen center and providing a single lone pair of electrons



ADPnO (1)

from the pnictogen center for complexation to the transition metal. This latter complexation mode is characterized by a planar ADPnO ligand with a pseudo-trigonalbipyramidal (Ψ-TBP) geometry at the pnictogen.

*To whom correspondence should be addressed.
†Visiting Research Scientist on leave from the Department of Chemistry, Southern Methodist University, Dallas, Texas 75275, U.S.A.
‡Contribution No. 4422

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Recent theoretical studies [8] have indicated that the stability of the 10-Pn-3 planar arrangement of the ADPnO molecules over their folded 8-Pn-3 alternatives is largely the result of the transfer of electron density from the organic ligand backbone to the central pnictogen. In effect, this transfer produces the second lone pair of electrons at the pnictogen as required for the 10-Pn-3 arrangement. For arsenic- and antimony-derived systems this rather simplistic picture is sufficiently accurate to describe the observed structures, their spectral features, and their chemistry. For the phosphorus analog (ADPO) the situation is more complicated.

In planar 10-P-3 ADPO the π-overlap of the out-of-plane *p*-orbital at phosphorus with the ligand π-system allows the return of electron density from phosphorus back to the ligand. This return of electron density will destabilize the planar (10-P-3) form and change the balance of energetics between the planar and folded forms of ADPO. At the SCF level, calculations predict that folded 8-P-3 ADPO should be the global minimum on the energy surface and that the planar structure is merely a local minimum [8]. Only with the inclusion of a correlation correction do the calculated energetics lead to a global minimum at the planar structure [8], in agreement with the experimental observations [1]. The importance of a correlation correction on the structure of ADPO has been interpreted in terms of a transfer of electron density from the electron-rich in-plane σ-system to the out-of-plane phosphorus *p*-orbital [8]. This added electron density at phosphorus is sufficient to compensate for losses due to π-interactions and thus maintain the preference for a planar geometry. If this interpretation is correct, loss in electron density at phosphorus (e.g. through coordination to Lewis acids) should give rise to a folding of the ADPO ring system. Indeed, this behavior has been previously observed in some platinum complexes of ADPO [1, 3].

The object of the current study is to examine the complexes formed between the ADPnO molecules and a single electrophile. In this way trends in coordination chemistry can be examined in light of theoretical expectations [8].

SUMMARY OF RESULTS

Insight is provided on the unusual ADPnO systems from the complexation chemistry observed with the pentamethylcyclopentadienylruthenium cation (Cp^*Ru^+) [9]. Both mono- (**2**) and disubstituted (**3**) adducts are available from the reaction of ADPO with tris(acetonitrile)(pentamethylcyclopentadienyl)-ruthenium triflate (**1**) as shown in Scheme 1. We have not observed substitution of the last acetonitrile even with excess ADPO. For these ADPO–Ru adducts only folded ring systems with tetrahedrally coordinated phosphorus centers are found. The antimony-derived ADSbO system forms a 3:1 adduct with **1** (Scheme 2). The 3:1 ADSbO–Ru adduct (**4**) is formed regardless of the starting material ratio used for the reaction. All three antimony centers in **4** are coordinated in a Ψ-TBP geometry.

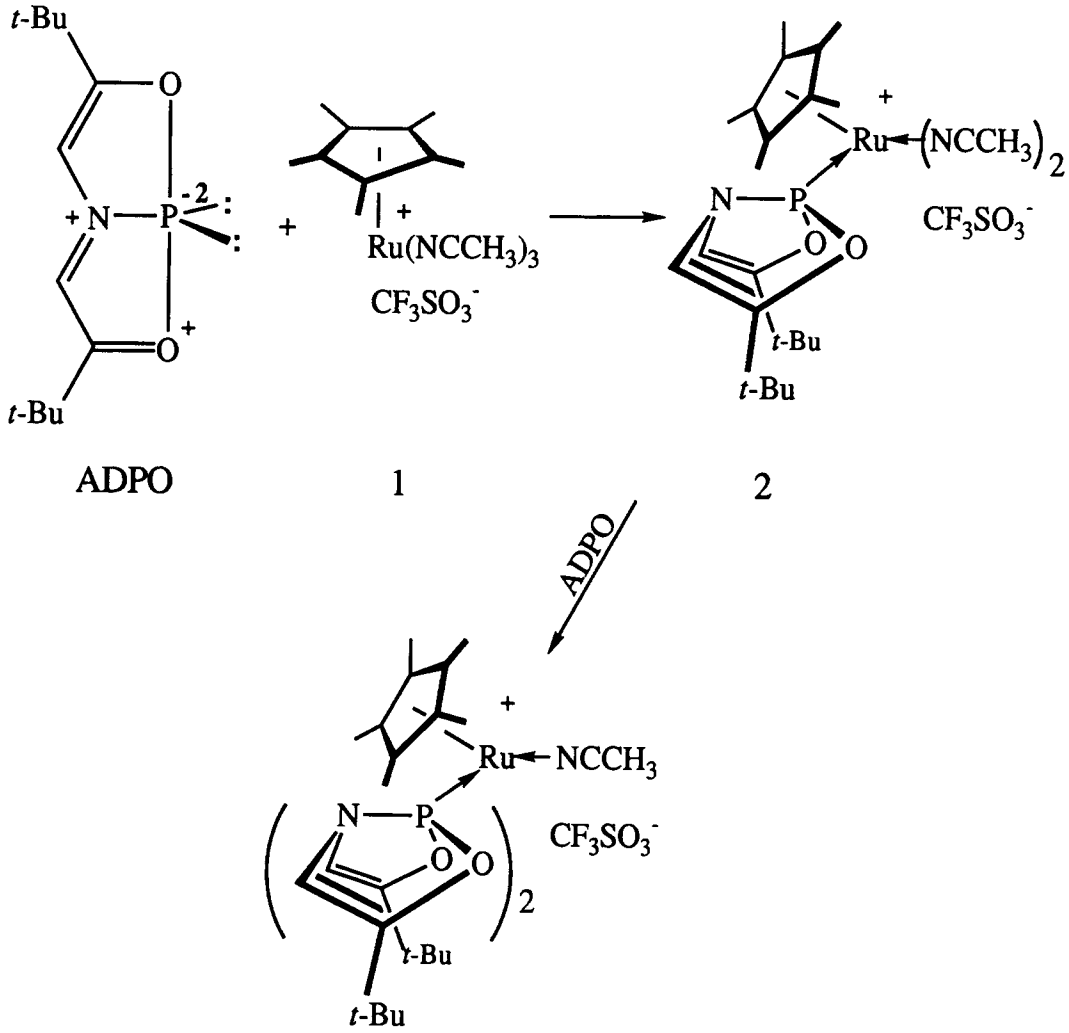
Although ADPO and ADSbO form adducts with the Cp^*Ru^+ moiety, which are related to those with platinum and palladium, the arsenic-derived ADAsO system exhibits an unprecedented coordination mode with the Cp^*Ru^+ unit. The reaction of ADAsO with **1** leads to complex formation accompanied by a *reversible* reorganization of the ADAsO unit. The ADAsO–Ru adduct (**5**) incorporates two Cp*Ru groups and a single ADAsO-derived fragment. The arsenic complex contains a trinuclear transition metal/main group metal ring (Scheme 3). Most remarkably, the cluster formation is reversible so that addition of acetonitrile leads to the formation of the initial ruthenium cation, **1**, and reassembly of the ADAsO ring system. There appears to be an intermediate (**6**) that is involved in the formation of **5** and incorporates only a single Cp^*Ru^+-derived fragment.

DISCUSSION

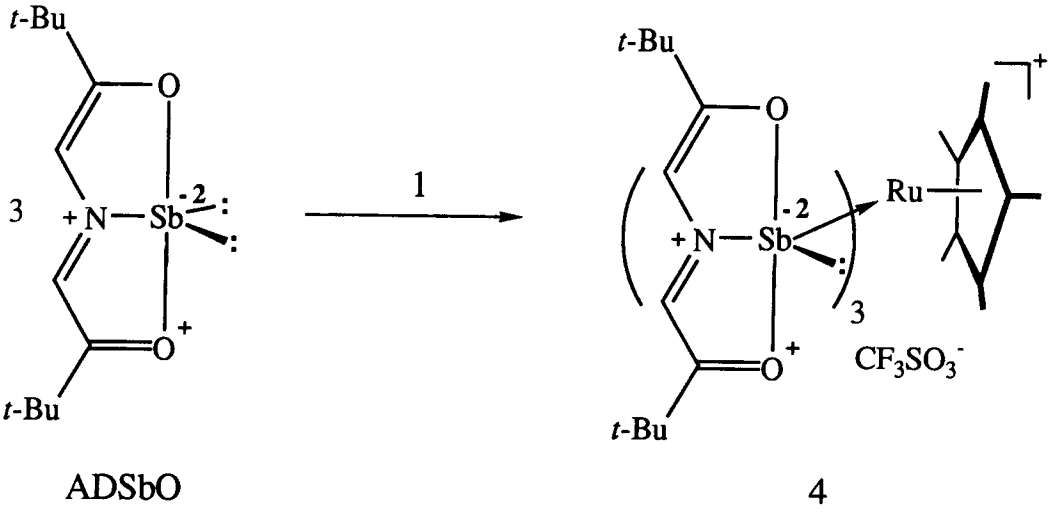
The reaction of ADPO with **1** proceeds in a stepwise fashion according to Scheme 1. Both the mono- and disubstituted products are isolable and well-characterized. The last acetonitrile is not displaced from the ruthenium center, even with excess ADPO. ADPO folds upon coordination to the Cp^*Ru^+ unit as we have previously observed with the platinum derivatives [1, 3].

The ^1H NMR spectrum of the 1:1 ruthenium–ADPO adduct (**2**) shows the presence of two acetonitriles and one ADPO unit per Cp^*Ru^+ group. This indicates that the ADPO unit is acting as a 2-electron donor to ruthenium (displacing one of the original acetonitriles from **1**). The ring proton resonances of the ADPO unit clearly indicate that a folded geometry has been attained in the ring system. The chemical shift of 5.79 ppm for these protons is very similar to those chemical shifts in previously reported adducts of ADPO in which ring folding and reduction of the tridentate ligand backbone has occurred [1]. The $^3J_{PH}$ coupling constant of 24.1 Hz is considerably larger than the value of 9.6 Hz observed for planar 10-P-3 ADPO and is characteristic of the folded and reduced ligand systems (e.g. in $(ADPO)_2PtI_2$ δ 5.95, $^3J_{PH}$ = 29.0 Hz) [1, 3]. The ^{13}C NMR spectrum supports the assignment of the organic ligand in the ADPO unit as reduced. The CO and CN carbons in this ligand resonate at 155.6 and 125.3 ppm respectively. These ^{13}C resonances are similar to those in many adducts of the ADPO system in which the ligand backbone is reduced and the phosphorus is involved in an 8-electron bonding system similar to the 8-P-4 arrangement in **2** [1].

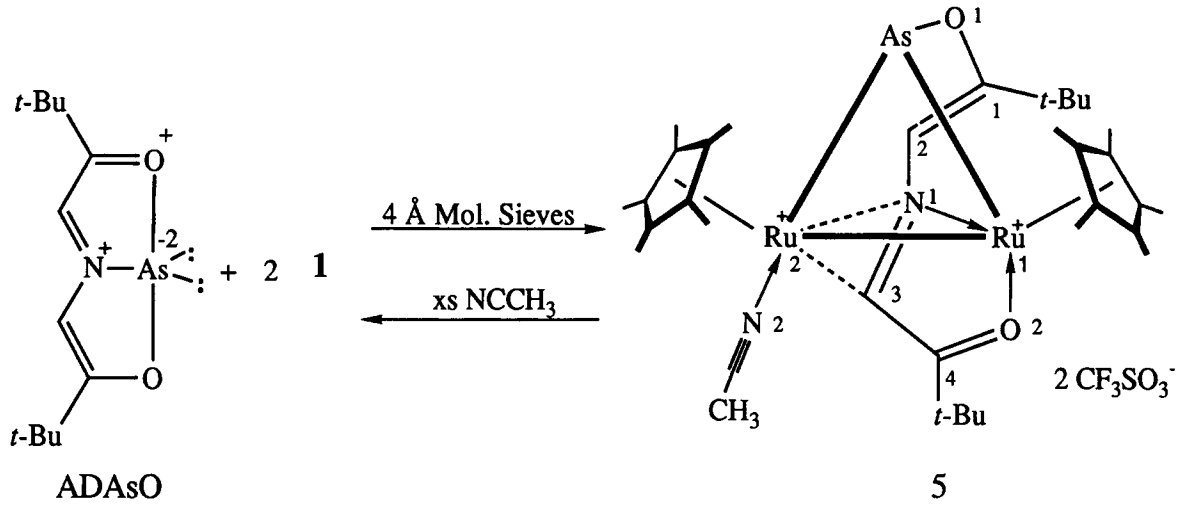
If two or more equivalents of ADPO are reacted



SCHEME 1



SCHEME 2



SCHEME 3

with **1**, a 2:1 adduct (**3**) is formed. Adduct **3** comprises the Cp^*Ru^+ group, an acetonitrile, two bent ADPO units, and a triflate counterion. As with **2**, the bending of the ADPO units in **3** is evident from the ^1H NMR shift of δ 5.82 for the ring proton. We were not able to incorporate a third ADPO to displace the final acetonitrile on **3**. There is likely to be considerable steric crowding about the ruthenium center in **2** due to the large Cp* and two folded ADPO units. This steric crowding may be the reason we do not observe the ready formation of a 3:1 adduct.

In contrast to the folded adducts formed between **1** and ADPO, ADSbO reacts with **1** to form a 3:1 adduct (**4**) (Scheme 2). The formation of **4** can be followed by ^1H NMR. Resonances due to **4** begin to appear very soon after mixing. We were not able to identify any resonances that could be attributed to a 1:1 or a 2:1 adduct. Apparently, successive replacements of acetonitrile ligands proceed faster for each additional ADSbO unit. It is interesting to speculate that the second lone pair at the antimony center of an ADSbO coordinated to Cp^*Ru^+ may assist in dissociation of an acetonitrile. This assisted dissociation could then be followed by addition of another ADSbO molecule.

The nature of the ADSbO units in **4** is clearly indicated by the ^1H and ^{13}C NMR spectra of the complex. The ring proton resonates at δ 8.74 and the ligand ring carbons appear at δ 190.1(CO) and 124.3(CN). These shifts point to a planar, oxidized ligand backbone similar to that in free 10-Sb-3 ADSbO [1]. Thus, a 10-Sb-4 bonding environment can be assigned at each antimony center.

The relative ease with which three ADSbO units can be coordinated to a Cp^*Ru^+ moiety compared to substitutions with ADPO led us to investigate the X-ray crystal structure of **4**. The structure of **4** is depicted in Figure 1 [10]. As expected, each of the ADSbO groups is nearly planar (fold angles about the Sb–N bonds are 1°, 4°, and 6°). Each ADSbO unit has a unique orientation with respect to the Cp* substituent. The three dihedral angles, $Cp^*_{(centroid)}$–Ru–Sb–N, are 13.8°, 146.8°, and 81.5°. The ADSbO groups are all bent away from the Cp* unit so that the three Sb–Ru–Sb angles are about 90°(±2). Crowding about the ruthenium is not only reflected in the Sb–Ru–Sb angles but also in the convex shape of the bonded face of the Cp* ring. On average the methyl groups on the cyclopentadienyl ring are 17.5 pm above the plane of the five ring atoms. The attachment of the three ADSbO

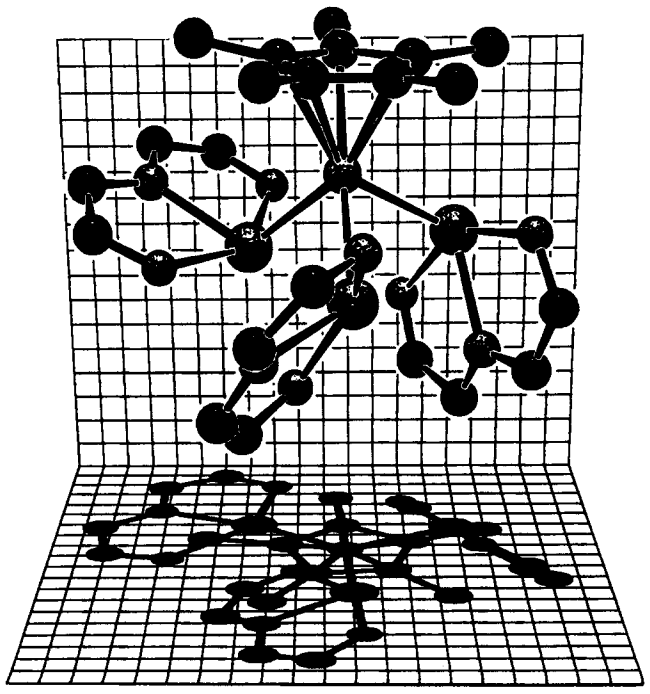


FIGURE 1 KANVAS [10] drawing of **4**; hydrogens and *t*-butyl carbons have been omitted for clarity.

groups is possible as a result of the length of the Sb–Ru bonds. Literature reports of Sb–Ru bonded compounds have given lengths around 262 pm [11–13]. The Sb–Ru bonds in **4** are actually slightly shorter (259 ± 1 pm) than the literature values for these trialkyl- or triarylstibine complexes. The lengths of the Sb–Ru bonds in **4** may reflect the relatively high *s*-orbital character of the approximate sp^2 hybrid orbital that describes an antimony lone pair in ADSbO compared to the sp^3 lone pair orbital of a typical stibine. Nevertheless, the Sb–Ru bonds in **4** are sufficiently long to allow the complexation of three ADSbO units. The geometry about the Sb centers can be described as pseudo-trigonalbipyramidal (Ψ-TBP). The apical positions of the trigonalbipyramids are occupied by the oxygens of the tridentate organic ligands. The equatorial sites are occupied by a nitrogen of the ligand, the ruthenium, and a second antimony lone pair. The N–Sb–Ru angles in the equatorial planes are 114°–128° for the three Sb centers. These equatorial angles are similar to the Pt–Sb–N angle (118.5°) we observed in a platinum complex of ADSbO [2]. Since the solid state orientation of each ADSbO unit of **4** is different, variation in the N–Sb–Ru angles is most likely a result of the unique steric compression felt by each ADSbO fragment. Various bond lengths in the ADSbO backbones (Table 1) are consistent with the NMR spectral indication that the organic ligand backbone is in its oxidized form.

When a solution of ADAsO and 2 equiv of **1** in THF is allowed to stand at ambient temperature for a few days, only a trace of liberated acetonitrile and a slight broadening of the initial resonances are observed by ^{1}H NMR. The addition of activated 4 Å molecular sieves to the reaction mixture (to absorb liberated acetonitrile) drives the reaction to completion with formation of **5**. The NMR spectra and elemental analysis of **5** indicate the presence of two Cp*Ru residues, an ADAsO derived fragment, an acetonitrile, and two triflate anions. The observation of two *t*-butyl and two ring proton resonances in the ^{1}H NMR spectrum indicates an asymmetric ligand backbone. The comparatively high field positions of the ring protons (δ 6.24 and 6.76) relative to the starting material indicates that the electronic environment of the organic ligand system originally found around arsenic has changed greatly. The ^{13}C chemical shifts of δ 116.7 and 218.4 for the CO carbons indicate that one terminus is carbonyl-like and the other is vinyl ether-like (consistent with the ^{1}H NMR spectrum). The presence of two distinct pentamethylcyclopentadienyl units in the NMR spectra points to two different environments for the ruthenium centers.

The structure of **5** was determined by X-ray crystallography and is shown in Figure 2 [10]. The presence of the 3-membered ring mixed metallocycle is evident with pentamethylcyclopentadienyl units capping each ruthenium. The original tridentate ligand from arsenic remains coordinated to arsenic, but through only a single oxygen. The liberated imine is coordinated to both ruthenium centers. One ruthenium is coordinated to lone pairs from both the carbonyl oxygen and imine nitrogen centers. An acetonitrile molecule and the C=N π-bond of the imine are coordinated to the second ruthenium. The overall metallocycle is a dication with two triflate counter ions. As such, a Ru–Ru single bond is required to achieve an electron count of 18e at each Ru center.

Selected bond lengths and angles are presented in Table 2. The 3-coordinate arsenic center is markedly pyramidal. The Ru–Ru and Ru–As distances are indicative of single bonds between these centers [14–16]. The localization of π-bonds in the organic ligand backbone is evident from the bond lengths along this ligand. The C_1–O_1 distance of 136.3 pm is consistent with a vinyl ether C–O bond. The C_1=C_2 bond is 132.9 pm, again suggesting a vinyl ether

TABLE 1 Selected Bond Lengths and Angles in **4**

Bond Length (pm)		Bond Angle (°)	
Sb–Ru	259.7(2), 258.1(2), 259.5(2)	Sb–Ru–Sb	91.0(2), 89.7(2), 88.0(2)
Ru–Cp*	186.3(cent.)	Ru–Sb–N	114.0(4), 114.0(4), 128.1(4)
Sb–O	220.7(13), 224.4(11)	Ru–Sb–O	98.9(4), 93.6(3)
	218.2(15), 224.6(13)		105.8(4), 90.7(3)
	217.1(12), 216.0(13)		100.4(3), 102.3(4)
Sb–N	216.2(15), 215.4(16), 213.2(14)	N–Sb(fold)	0.87, 4.20, 5.96
C–O	129.8(22), 127.3(18)	C–C–O	121(2), 118(1)
	123.4(27), 131.8(21)		124(2), 119(2)
	131.5(20), 130.0(24)		120(2), 117(2)
C–N	137.3(22), 134.4(22)	C–C–N	114(2), 114(2)
	137.1(26), 135.9(23)		111(2), 115(2)
	133.6(23), 133.7(23)		114(2), 116(2)
C–C	135.9(24), 142.7(24)	O–Sb–O	143.8(4), 145.8(5), 146.4(5)
	141.7(31), 137.7(25)	C–N–C	123(2), 124(2), 124(2)
	134.8(25), 141.2(26)	Cp*–Ru–Sb–N	13.8, 146.8, 81.5

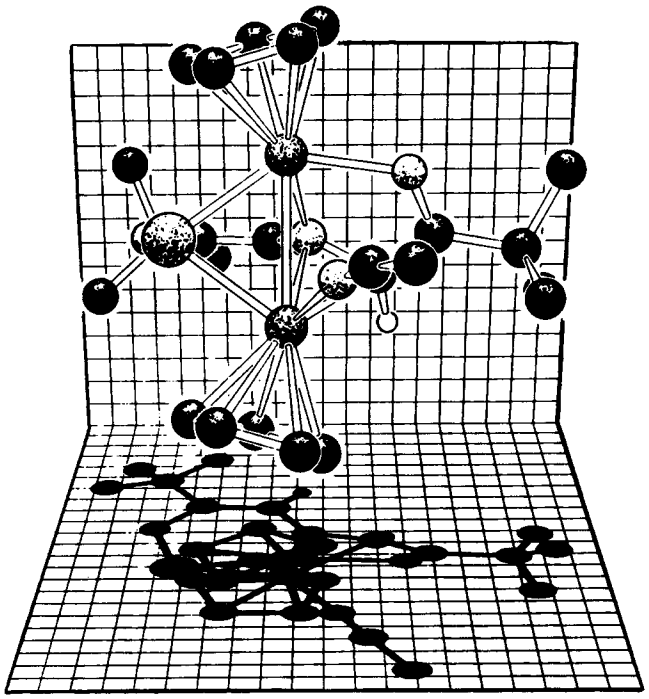


FIGURE 2 KANVAS [10] drawing of **5**; *t*-butyl hydrogens and Cp* methyls have been omitted for clarity.

moiety. Also, as expected for a vinyl ether, the dihedral angles about the $C_1{=}C_2$ bond indicate an essentially planar fragment. These features for the vinyl ether moiety are visually apparent in Figure 2. The left-rear portion of the lower plane in Figure 2 bears the shadow cast by the vinyl ether fragment. The *t*-butyl, O, H, and N substituents on the $C_1{=}C_2$ double bond can be easily identified. The direct view of **5** is almost perfectly in the plane of the vinyl ether group that is partially obscured by the arsenic on the left and by the Ru–Ru bond on the right. This direct view is also perpendicular to the As–Ru–Ru plane. It can be seen that the plane of the three metals is orthogonal to the vinyl ether plane. It is interesting that the arsenic atom also lies in the plane of the vinyl ether. Since the entire As–O–C–C–N fragment is planar and cisoid, the nitrogen has a closest approach to the arsenic of 278.2 pm. This is the same arrangement these atoms have in the initial ADAsO system except that the As–N distance is initially much shorter (~184 pm) [1]. This much greater As–N distance in **5** is largely traceable to the increased valence angles at O_1 (~14°), C_1 (~8°), and C_2 (~9°) for **5** relative to ADAsO. Nonetheless this 5-atom group still bears a vague structural relation to the initial ADAsO molecule. Beyond this group of atoms the organic ligand backbone begins to deviate from planarity. There is a 150° dihedral angle between the vinyl ether fragment and the imine fragment (C_1–C_2–N_1–C_3). The imine moiety itself is twisted about the $C_3{=}N_1$ double bond to give a 143° dihedral angle (C_2–N_1–C_3–C_4). The $C_3{=}N_1$ bond distance is short (136.5 pm) as would be expected for such an imine. The π-complexation of the imine to Ru_2 may give added flexibility to the $C_3{=}N_1$ interaction and help ease the observed twist about $C_3{=}N_1$. The N_1–C_3–C_4–O_2 dihedral is small (8°) so that the $C_4{=}O_2$ carbonyl is conjugated to the imine ($C_3{=}N_1$). The C_3–C_4 distance of 141 pm is supportive of some additional π-interaction between these centers. The $C_4{=}O_2$ distance (128.4) clearly identifies this bond as carbonyl-like. The coordination of Ru_1 to the carbonyl oxygen, O_2, occurs through an in-plane oxygen lone pair. Thus, the C_3–C_4–O_2–Ru_1 dihedral angle is 9°. These descriptions of the organic ligand backbone centers are strongly supported by the four ^{13}C NMR resonances in the backbone. C_1 and C_2 resonate at 166.7 and 83.3 ppm respectively (vinyl ether-like). The C_3 and C_4 resonances of 137.4 and 218.4 also suggest the imine and carbonyl nature of these centers.

The resilience of the ADAsO fragment is nicely demonstrated by its reassembly upon displacement from the ruthenium centers with additional acetonitrile. Like the forward reaction, this reversal takes place smoothly at room temperature. The forward and reverse reactions may proceed through an intermediate in which only one ruthenium center is complexed to an asymmetric ADAsO fragment with no additional acetonitrile. A potential intermediate has been isolated and characterized by its ^1H NMR spectrum and elemental analysis. The role of this material as an intermediate is suggested by

TABLE 2 Selected Bond Lengths and Angles in **5**

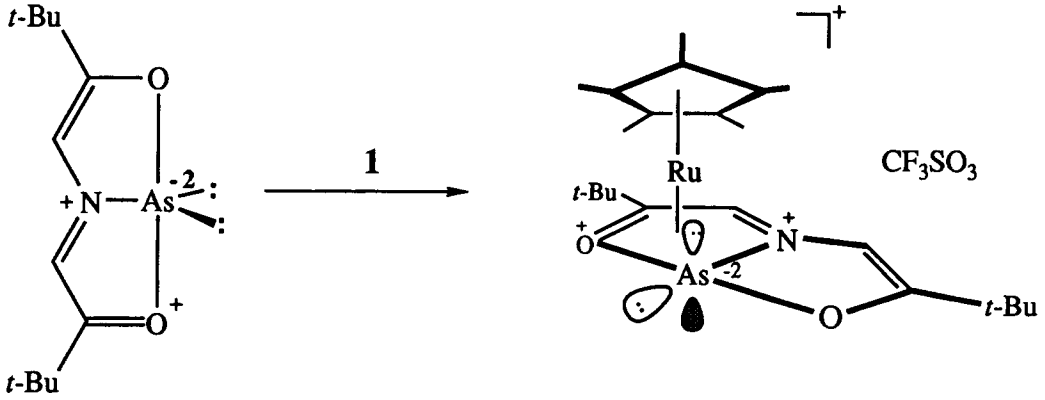
Bond Length (pm)				Bond Angle (°)			
Ru–Ru	285.5(1)	Ru_1–As	242.4(1)	Ru–As–Ru	71.54(3)	Ru_1–As–O_1	102.3(2)
Ru_2–As	245.9(1)	Ru_1–O_2	209.6(6)	Ru_2–As–O_1	102.4(1)	Ru_1–Ru_2–As	53.66(3)
Ru_1–N_1	207.2(6)	Ru_1–Cp*	184.4(cent.)	Ru_2–Ru_1–As	54.80(2)	Ru_2–Ru_1–N_1	48.3(2)
Ru_2–N_1	213.7(6)	Ru_2–C_3	223.9(9)	Ru_1–Ru_2–N_1	46.4(1)	Ru_1–N_1–Ru_2	85.4(2)
Ru_2–N_2	210.2(9)	Ru_2–Cp*	187.3(cent.)	Ru_2–C_3–C_4	108.3(6)	As–O_1–C_1	127.8(4)
As–O_1	182.0(5)	O_1–C_1	136.3(8)	O_1–C_1–C_2	122.8(7)	C_1–C_2–N_1	122.6(7)
C_1–C_2	132.9(10)	C_2–N_1	141.9(9)	C_2–N_1–C_3	119.7(6)	N_1–C_3–C_4	116.3(7)
N_1–C_3	136.5(10)	C_3–C_4	141.0(11)	C_3–C_4–O_2	114.9(7)	Ru_1–O_2–C_4	116.2(5)
C_4–O_2	128.4(9)						

the observation that further reaction with **1** leads to the formation of **5** (even without molecular sieves). Transient NMR resonances attributable to this intermediate can also be identified in reactions forming **5**. While X-ray crystal structure determination on the intermediate has not been possible thus far, the ^{1}H NMR spectrum suggests a possible structure for this unstable intermediate, **6**. The ^{1}H NMR spectrum of **6** indicates a 1:1 ratio of Cp*Ru to ADAsO fragments. Unlike **5**, there is no remaining acetonitrile in the complex. The ^{19}F NMR shows a single triflate resonance. This composition is also supported by the elemental analysis. The ^{1}H NMR further indicates asymmetry in the tridentate ligand backbone. The *t*-butyl groups and ring protons are both present as two sets of two resonances. The ring protons resonate at 8.0 and 9.4 ppm. The downfield positions of these ring proton resonances are not consistent with a vinyl ether fragment as was found in **5** but rather suggests a largely intact ADAsO ring system. The Cp*Ru cation usually gives complexes in which an 18-electron configuration is found for the ruthenium [9, 17]. In this case, although participation of the triflate counterion cannot be ruled out, it seems reasonable that the ADAsO fragment could provide the six electrons necessary at the ruthenium center (Scheme 4). As such, this intermediate may be an η^5 π-complex involving a single ring of the ADAsO moiety (**6**). Other η^5 complexes from Cp^*Ru^+ and 5-membered ring aromatic heterocycles have been reported [17]. If this intermediate does have a structure like **6**, it is easy to imagine how antarafacial coordination of a second Cp^*Ru^+ group to the second ADAsO 5-membered ring with subsequent rearrangement could give rise to **5**. Work is continuing to obtain crystals of **6** to determine its X-ray structure since this would represent a new coordination mode for ADPnO ring systems.

Along certain pathways it is possible to transfer the Cp^*Ru^+ unit from one ADPnO group to another (ADPn'O). The preliminary reactions we have observed thus far indicate a reactivity pattern analogous to the pattern that we had previously observed for transfer of *o*-chloranil units between ADPnO molecules [1]. Either ADPO or ADSbO will react with **5** to liberate ADAsO and form ADPO- or ADSbO-derived Cp^*Ru^+ complexes. The ADSbO adduct, **4**, will react very slowly with ADPO to release some ADSbO and form a new mixed complex with both planar ADSbO and folded ADPO units coordinated to the Cp^*Ru^+ unit. From tentative ^{1}H NMR data this new complex appears to have the composition $[Cp^*Ru(ADPO)(ADSbO)_2]^+$. This reaction actually appears to involve an equilibrium and may not proceed to completion. This new mixed pnictogen complex has been observed only in solution and has not been fully characterized. The ADPO complex, **3**, does not react with either ADSbO or ADAsO. The ADSbO adduct **4** does not react with ADAsO. Thus an approximate order of reactivity of ADPnO molecules toward the Cp^*Ru^+ electrophile can be constructed (ADPO > ADSbO >> ADAsO).

CONCLUSION

ADPO reacts with the ruthenium-centered electrophile, **1**, to give 8-P-4 complexes of the folded ADPO ring system. Complex formation proceeds in a stepwise fashion, and both mono- and bis-(ADPO) adducts have been isolated and characterized. The folding of the ADPO moieties in complexes **2** and **3** is in accord with previous reactions of ADPO with electrophiles that give adducts appearing to be derived from the hypothetical folded 8-P-3 ADPO rather than planar 10-P-3 ADPO. The folding of ADPO and reduction of the organic ligand backbone upon complexation with electrophiles is most likely the result of combined electronic and steric factors. The smaller size of the phosphorus atom relative to ar-



ADAsO **6**

SCHEME 4

senic and antimony leads to a preference for the less sterically congested 8-P-4 arrangement (tetrahedral geometry) over the 10-P-4, pseudo-trigonalbipyramidal geometry. Ab initio calculations [8] have indicated that the stability of planar 10-P-3 ADPO over its folded 8-P-3 counterpart is somewhat marginal and that a loss of electron density at phosphorus could lead to a reversal of stabilities. Indeed, we have shown that complexation of phosphorus with Cp^*Ru^+ leads to adducts that are derived from the 8-P-3 arrangement, in accord with theoretical models.

The antimony lone pair electrons in ADSbO are excellent donors toward the Cp^*Ru^+ electrophile, and a 3:1 adduct is readily formed. The second lone pair of electrons at antimony centers of coordinated ADSbO units has previously been observed to be stereochemically active [2]. However, there has not been any indication of chemical reactivity of this pair of electrons. The apparent increasing ease with which successive ADSbO units can be coordinated to **1** suggests that the second lone pair of electrons at the antimony center may have a chemical role to play.

Finally, the type of complex formation demonstrated between Cp^*Ru^+ and ADAsO is radically different from the types of complexes we have previously described between ADPnO molecules and Pt and Pd centers [1–3]. The Cp^*Ru^+ center is an excellent electrophile for examining the systematic variations in ADPnO chemistry. In a sense, the arsenic chemistry seems to fit nicely between that of phosphorus and antimony. ADSbO behaves as if there were two lone pairs of electrons at the antimony center, in accord with theoretical models [8]. Complexes of ADSbO and metals show the expected Ψ-TBP geometry at antimony with a stereochemically active lone pair of electrons remaining at the antimony center. Theoretical models [8] have predicted that 10-P-3 ADPO is energetically close to its 8-P-3 analog, and a small change in electron density at phosphorus can lead to a reversal of the energy ordering. In accord with this expectation ADPO-metal complexes exhibit the folded, 8-P-3 derived arrangement as a result of loss of electron density from phosphorus to the metal. The ADAsO system shows a much more complicated coordination chemistry in which both the arsenic center and the ligand backbone participate. This may be consistent with an interaction between arsenic and the ligand backbone that is intermediate between those of the phosphorus and antimony analogs. Unlike the antimony center in ADSbO, which appears to be a good electron donor independent of the oxidized ligand backbone, and unlike the phosphorus in ADPO, which can also donate a pair of electrons for dative bonding but suffers a geometric rearrangement and reduction of the ligand backbone, the arsenic-derived system maintains an oxidized ligand backbone but suffers some σ-reorganization.

Work is continuing to expand our understanding of the coordination chemistry of these unusual pnictogen systems.

EXPERIMENTAL

Reactions and manipulations were carried out under an atmosphere of dry nitrogen, either in a Vacuum Atmospheres drybox or using standard Schlenk techniques. Solvents were dried (using standard procedures) [18], distilled, and deoxygenated prior to use, unless otherwise indicated. Glassware was oven-dried at 160°C overnight. Molecular sieves were activated, stored in the drybox, and retreated under vacuum prior to use. Proton NMR spectra were recorded on a General Electric QE-300 spectrometer. ^{13}C and ^{31}P NMR spectra were recorded on a Nicolet NT-300WB spectrometer. Chemical shifts are reported in ppm (δ) with positive values downfield of the reference (^1H, ^{13}C: Me_4Si; ^{31}P: ext. 85% H_3PO_4; ^{19}F: $CFCl_3$). Melting points were obtained on a Thomas-Hoover capillary apparatus and are uncorrected. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY, and are within 0.40% of theoretical, unless otherwise stated.

The starting materials, $[Cp^*Ru(CH_3CN)_3]^+ CF_3SO_3^-$ (**1**) [9] and ADPnO [1], were synthesized as described previously.

$[Cp^*Ru(ADPO)(CH_3CN)_2]O_3SCF_3$ (**2**)

A solution of **1** (70 mg, 0.14 mmol) in CD_2Cl_2 (1 mL) was treated with a solution of ADPO (33 mg, 0.14 mmol). The resulting mixture was allowed to stand for 18 h, yielding an orange/yellow solution, with a trace amount of precipitate. The mixture was filtered, and sufficient pentane added to the filtrate to precipitate the product. The solid was separated, washed with pentane, and pumped dry to give **2** as an air-sensitive off-white solid: 92 mg (93%); mp 57–75°C (dec). NMR spectra (CD_2Cl_2): ^1H, δ 1.15 (s, 18 H), 1.70 (d, $^4J_{PH}$ = 3.2 Hz, 15 H), 2.39 (d, $^5J_{PH}$ = 1.5 Hz, 6 H), 5.79 (d, $^3J_{PH}$ = 24.1 Hz, 2 H); $^{13}C\{^1H\}$, δ 4.4 (CH_3CN, s), 9.8 ($CH_3(Cp^*)$, s), 27.6 ($C(CH_3)_3$, s), 32.4 ($C(CH_3)_3$, d, $^3J_{PC}$ = 4.1 Hz), 90.7 ($C(Cp^*)$, d, $^2J_{PC}$ = 4.2 Hz), 113.9 (CH_3CN, s), 125.3 (CNP, s), 155.6 (COP, d, $^2J_{PC}$ = 6.0 Hz); $^{31}P\{^1H\}$, δ 198; ^{19}F, δ −78.3. Anal. Calcd. for ($C_{27}H_{41}F_3N_3O_5PRuS$): C, 45.75; H, 5.83; N, 5.93. Found: C, 45.14; H, 5.66; N, 5.59.

$[Cp^*Ru(ADPO)_2(CH_3CN)]O_3SCF_3$ (**3**)

A solution of **1** (50 mg, 0.098 mmol) in CD_2Cl_2 (1 mL) was treated with a solution of ADPO (48 mg, 0.20 mmol). The resulting mixture was allowed to stand for 48 h, yielding a pale yellow solution, with a trace amount of precipitate. The mixture was filtered, and pentane was added to the filtrate to pre-

cipitate the product. The solid was separated, washed with pentane, and pumped dry to give **3** as an air-sensitive off-white solid: 71 mg (80%); mp 155–159°C (dec). NMR spectra (CD_2Cl_2): ^1H, δ 1.13 (s, 36 H), 1.79 (t, $^4J_{PH}$ = 3.2 Hz, 15 H), 2.27 (br s, 3 H), 5.82 (comp. m, 4 H); $^{13}C\{^1H\}$, δ 4.9 (CH_3CN, s), 10.0 ($CH_3(Cp^*)$, s), 27.5 ($C(CH_3)_3$, s), 32.4 ($C(CH_3)_3$, t, $^3J_{PC}$ = 2.4 Hz), 97.3 ($C(Cp^*)$, t, $^2J_{PC}$ = 2.9 Hz), 115 (CH_3CN, br), 125.5 (CNP, s), 155.9 (COP, t, $^2J_{PC}$ = 2.8 Hz); $^{31}P\{^1H\}$, δ 201; ^{19}F, δ −79.4. Anal. ($C_{37}H_{58}F_3N_3O_7P_2RuS$): C, H, N.

$[Cp^*Ru(ADSbO)_3]O_3SCF_3$ (4)

A solution of **1** (200 mg, 0.394 mmol) and ADSbO (392 mg, 1.18 mmol) in CH_2Cl_2 (10 mL) was stirred at 23°C. After 0.5 h the solution was dark green. The volatiles were then removed in vacuo. ^1H NMR spectra indicated the reaction not to be complete. The residue was redissolved in CH_2Cl_2 with additional ADSbO (263 mg, 0.793 mmol) and stirred for an additional 18 h. Pentane was added to precipitate the product. The solid was then separated, washed with pentane, and dried to yield fine, black, air-sensitive crystals of **4**: 381 mg (70%); mp 235–240°C (dec). NMR spectra (CD_2Cl_2): ^1H, δ 1.30 (s, 54 H), 1.48 (s, 15 H), 8.74 (s, 6 H); $^{13}C\{^1H\}$, δ 10.7 ($CH_3(Cp^*)$), 28.4 ($C(CH_3)_3$), 40.4 ($C(CH_3)_3$), 89.0 ($C(Cp^*)$), 124.3 (CN), 190.1 (CO); ^{19}F, δ −77.7. Anal. ($C_{47}H_{75}F_3N_3O_9RuSSb$): C, H, N.

$[(Cp^*Ru)_2(ADAsO)(CH_3CN)](O_3SCF_3)_2$ (5)

Under an inert atmosphere, forty 4 Å molecular sieves (4–8 mesh) were added to a solution of ADAsO (100 mg, 0.351 mmol) and **1** (357 mg, 0.702 mmol) in THF-d_8 (5 mL). The mixture was allowed to stand for 3 days, during which time a precipitate formed. During this time the color of the solution turned from dark green to red/brown. The mixture was then filtered and the residue washed with THF and allowed to dry. Physical separation of the crystalline product from the sieves yielded pure **5** (253 mg, 66%) as maroon crystals; mp 190–200°C (dec); NMR spectra (CD_2Cl_2): ^1H δ 1.31 (s, 9 H), 1.44 (s, 9H), 1.74 (s, 30H), 2.85 (s, 3H), 6.24 (s, 1H), 6.76 (s, 1H); $^{13}C\{^1H\}$ δ 6.4 (CH_3CN), 9.3, 9.6 (CH_3, Cp^*), 27.9, 28.8 ($C(CH_3)_3$), 37.3, 42.9 ($C(CH_3)_3$), 83.3 (C—N), 96.6, 103.4 (C, Cp^*), 111.8 (CH_3CN), 137.4 (C=N), 166.7 (CO), 218.4 (C=O); ^{19}F δ −79. Anal. ($C_{36}H_{53}AsF_6N_2O_8Ru_2S_2$): C, H, N.

$[(Cp^*Ru)(ADAsO)](O_3SCF_3)$ (6)

In a procedure similar to that described above for **5**, ADAsO (100 mg, 0.351 mmol) and **1** (178 mg, 0.350 mmol) are mixed in 5 mL THF along with forty 4 Å molecular sieves (4–8 mesh). After 4 days the supernatant was filtered off and concentrated to about 2 mL. Pentane (10 mL) was carefully layered over the THF solution and the sample was stored at −30°C overnight. The solid that formed was collected by filtration and washed with pentane to yield 62 mg of a brown microcrystalline solid. ^1H NMR (THF-d_8) δ 1.27 (s, 9H), 1.37 (s, 9H), 1.79 (s, 15H), 8.00 (s, 1H), 9.40 (s, 1H); ^{13}C NMR (THF-d_8) δ 10.7 (CH_3, Cp^*), 28.5, 28.7 ($C(CH_3)_3$), 89.8, 95.5 (CN); ^{19}F NMR (THF-d_8) δ −80. Anal. Calcd. for ($C_{23}H_{35}AsF_3NO_5RuS$): C, 41.20; H, 5.26; N, 2.09 Found: C, 40.47; H, 5.27; N, 1.76.

Reaction of **5** *with* CH_3CN

In an NMR tube, a CD_2Cl_2 solution containing **5** (8 mg, 0.007 mmol) was treated with one drop of CH_3CN (approx. 10 mg, 0.3 mmol). The ^1H NMR spectrum, taken shortly after CH_3CN addition, showed only the presence of **1**, uncomplexed ADAsO, and CH_3CN.

Reaction of **6** *with* **1**

An 85 mg (0.13 mmol) sample of **6** was treated with **1** (0.081 g, 0.16 mmol) in THF-d_8 (6 mL). The mixture was allowed to stand for 4 days. The crystals that precipitated were separated, washed with THF, and pumped dry, yielding spectroscopically pure **5** (0.041 g).

Reaction of **5** *with ADSbO*

In an NMR tube, a mixture of **5** (10 mg, 0.0091 mmol) and ADSbO (21 mg, 0.063 mmol) was dissolved in CD_2Cl_2. Resonances due to **5** immediately disappeared. Within a day, the spectrum showed the presence of only **4**, ADSbO, and ADAsO.

Reaction of **5** *with ADPO*

In an NMR tube, a mixture of **5** (10 mg, 0.0091 mmol) and ADPO (15 mg, 0.062 mmol) was dissolved in CD_2Cl_2. Resonances due to **5** immediately disappeared. Within a day, the spectrum showed the presence of **3**, ADPO, and ADAsO, as well as peaks due to an unidentified compound.

Reaction of **3** *with ADSbO*

In an NMR tube, a mixture of **3** (10 mg, 0.011 mmol) and ADSbO (15 mg, 0.045 mmol) was dissolved in CD_2Cl_2. Resonances due to **3** and ADSbO showed no change from the pure starting material after 2 days.

Reaction of **4** *with ADPO*

In an NMR tube, a mixture of **4** (20 mg, 0.049 mmol) and ADPO (12 mg, 0.049 mmol) was dissolved in CD_2Cl_2. After 1 day there was no observable change in the ^1H NMR spectrum and only the starting materials could be identified. After a week the ^1H NMR spectrum showed the presence of **4**, ADPO, and ADSbO, as well as peaks due to an unidentified compound: δ 1.02 (s, 18 H), 1.53 (s, 18 H), 1.54 (s, 18 H), 5.53 (d, $^3J_{PH}$ = 25.8, 2 H), 8.85 (s, 2 H). These new peaks continued to increase in intensity with time up to about 2 weeks. The new peaks are consistent with a structure of the composition $[Cp^*Ru(ADPO)(ADSbO)_2]^+$. An additional resonance for the Cp^*CH_3's in the new complex was not immediately evident, but there was a slight shoulder on the downfield side of the Cp^* resonance of **4**.

X-ray Crystal Structure of **4**

Formula: $C_{50}H_{60}Sb_3F_3N_3O_9RuS$, orthorhombic, space group $Pna2_1$ (No. 33), a = 2174.9(4), b = 2213.2(2), c = 1191.6(6) pm; T = −100°C, Z = 4, FW = 1402.46, D_c = 1.624 g/cm^3, μ (Mo) = 17.55 cm^{-1}; Crystal description: black, needle (0.15 × 0.13 × 0.38 mm) grown from hexane diffusion into a CH_2Cl_2 solution of **4**. A total of 6283 reflections were collected, 4.1° ≤ 2θ ≤ 52.0°, on a Syntex R3 diffractometer with graphite monochromator using Mo-K_α radiation (λ = 71.073 pm). With 3328 unique reflections of intensity greater than 3.0 σ, the structure was solved by automated Patterson analysis (PHASE) and standard difference Fourier techniques. The final R factors were R = 0.060, R_w = 0.049. The final difference Fourier showed the largest residual density to be 1.00 e/Å^3, near the triflate. Atomic coordinates, bond lengths, angles, and thermal parameters are available in supplementary material.

X-ray Crystal Structure of **5**

Formula: $C_{36}H_{53}AsF_6N_2O_8Ru_2S_2$, monoclinic, space group $P2_1/c$ (No. 14), a = 1136.9(2), b = 2172.5(4), c = 1736.5(3) pm, β = 90.38(2)°; T = −100°C, Z = 4, FW = 1097.07, D_c = 1.699 g/cm^3, μ (Mo) = 16.22 cm^{-1}; Crystal description: black, irregular rectangle (0.20 × 0.11 × 0.36 mm) grown from pentane diffusion into a CH_2Cl_2 solution of **5**. A total of 9623 reflections were collected, 4.0° ≤ 2θ ≤ 53.0°, on a Syntex R3 diffractometer with graphite monochromator using Mo-K_α radiation (λ = 71.073 pm). With 5123 unique reflections of intensity greater than 3.0 σ, the structure was solved by automated Patterson analysis (PHASE) and standard difference Fourier techniques. The final R factors were R = 0.054, R_w = 0.048. The final difference Fourier showed the largest residual density to be 2.03 e/Å^3, midway between atoms Ru_2, N_2, C_3, and C_4. Atomic coordinates, bond lengths, angles, and thermal parameters are available in supplementary material.

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SUPPLEMENTARY MATERIAL AVAILABLE

A complete description of the X-ray crystallographic structure determinations on **4** and **5** has been deposited with the Cambridge Crystallographic Data Centre.

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