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A Photochemical Route to a Square Planar, Ruthenium(IV)-bis(Imide)

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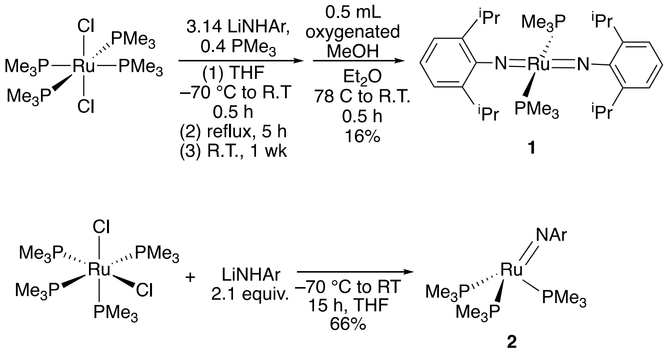
The square planar, ruthenium(IV) bis(imide) *trans*-Ru(NAr)$_2$(PMe$_3$)$_2$ can be prepared photochemically from a Ru(II) tetrazene. Additionally, we report reactivity of the Ru(IV) bis(imide) species, similar to that of the osmium derivative. Attempts to change both imide group and phosphine substituents are presented, which led to alternative reactivity.

In 1992, Wilkinson and coworkers reported the synthesis of a unique square planar, d^4, Ru(=NAr)$_2$(PMe$_3$)$_2$ (**1**) with trans imide groups , where Ar = 2,6-diisopropylphenyl.[1] The synthesis of this complex, as reported, starts with ruthenium(II) *trans*-RuCl$_2$(PMe$_3$)$_4$. Upon addition of excess LiNHAr, a proposed Ru(II) bis(amide) intermediate species is formed *in situ* over the course of 1 week. The proposed bis(amide) intermediate is then converted to **1** in 16% yield on exposure to oxygenated methanol (Scheme 1).

In related chemistry, Schrock and coworkers prepared the Os(=NAr)$_2$(PMe$_3$)$_2$ analogue through a very different route.[2, 3] They found that OsO$_4$ reacted with ArNCO to give Os(NAr)$_3$, which gave Os(=NAr)$_2$(PMe$_3$)$_2$ on reaction with phosphines.

Previously,[4] we reported that switching from *trans*- to *cis*-RuCl$_2$(PMe$_3$)$_4$, where the higher trans-labilizing ability of the phosphines greatly accelerated substitution of the chlorides,[5] led to much faster reactivity with the lithium amide (Scheme 1). From the reaction of *cis*-RuCl$_2$(PMe$_3$)$_4$ with 2 equiv of LiNHAr, we isolated the interesting Ru(NAr)(PMe$_3$)$_3$ (**2**), which is distorted from C_{3v}.[4] In later work, M(NAr)(PR$_3$)$_3^{0/+}$ complexes have been generated and characterized where M = Fe and Ru, to examine differences in electronic structure between the 1st and 2nd row elements in these systems.[6]

Here, we report that Wilkinson and coworkers' Ru(=NAr)$_2$(PMe$_3$)$_2$ (**1**) square planar complex can be prepared photochemically from the tetrazene Ru(N$_4$Ar$_2$)(PMe$_3$)$_3$. The tetrazene was prepared in high yield from our previously reported Ru(NAr)(PMe$_3$)$_3$ (**2**) and N$_3$Ar.



Scheme 1. (*top*) Synthetic procedure for the preparation of Ru(=NAr)$_2$(PMe$_3$)$_2$ (**1**) as reported by Wilkinson and coworkers. (*bottom*) Synthesis of ruthenium(II) Ru(NAr)(PMe$_3$)$_3$ (**2**).

In 1993, Hansert and Vahrenkamp reported the formation of a symmetric Fe(CO)$_3$(1,4-diphenyltetrazene) species, which upon exposure to UV light eliminated N$_2$ and formed dimeric {Fe(CO)$_3$}$_2$(μ-PhNNPh).[7] Several additional examples of N$_2$ elimination from metal-tetrazene species include Zr, Cr, V, and Fe complexes that produce mono- or bis-imido species.[8-10] These examples are thermally driven or result from spontaneous redox reactions at reduced temperatures.

Azides used in conjunction with low oxidation state metals are a common method for production of imide ligands; for recent examples involving Group-8 metals, one can see reports with Fe species by the Power group and the Deng group.[11, 12] Additionally, Wilkinson and coworkers had previously reported isolation of several Ru, Rh, and Ir tetrazene species with neutral ancillary ligands.[13, 14] Tetrazenes commonly result when metal imide complexes are treated with organic azide, but loss of N$_2$ from a tetrazene to form an isolable bis(imide) complex is uncommon. There is, however, a recent example from Arnold, Bergman, and coworkers where a niobium tetrazene complex undergoes this reaction thermally.[15]

In a similar manner to the reported reaction of Ru(NAr$^{tBu}{}_3$)(η_6-cymene) with N$_3$Mes,[13] we found that **2** reacts with a variety of different azides, N$_3$R, where R = 2,6-^{i}Pr$_2$C$_6$H$_3$ (Ar), mesityl (Mes), or 2,4,6-^{i}Pr$_3$C$_6$H$_2$ (Ar*), to give several

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Electronic Supplementary Information (ESI) available: Synthetic details for new complexes, characterization data, and images of spectra. Structural data has been uploaded in cif format to the Cambridge Crystallographic Database: CCDC 1895000-1895005, 1895272. See DOI: 10.1039/x0xx00000x different substituted tetrazene species **3a-c** (Figure 1) in moderate to high yield. This procedure also appears to supply the tetrazene when R = TMS; however, the resulting tetrazene species is relatively unstable, exhibiting both thermal decomposition and decomposition upon exposure to ambient light.

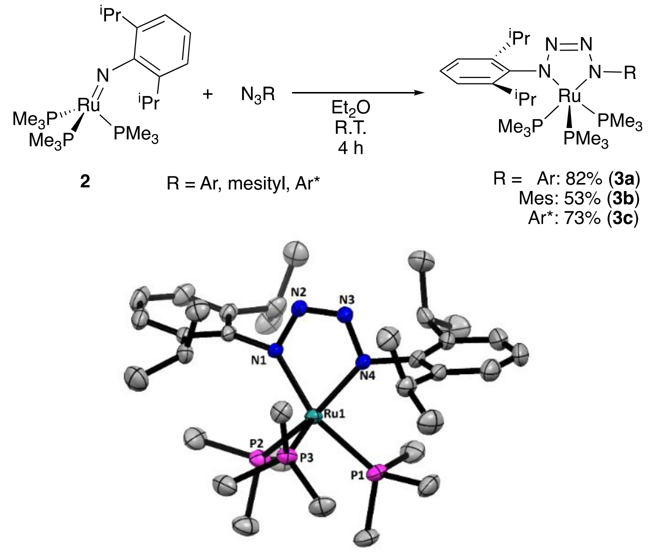


Figure 1. General synthesis of Ru{N_4(Ar)R}$(PMe_3)_3$ (**3**) from **2** and N_3R and the structure from single crystal X-ray diffraction of $Ru(N_4Ar_2)(PMe_3)_3$ (**3a**). Ellipsoids are shown at 50% probability level, and hydrogens in calculated positions are omitted.

The relatively stable aryl-substituted tetrazenes, **3a-c,** provide nearly a square-pyramidal geometry around ruthenium by X-ray diffraction. Here N1, N4, P1, and P3 come quite close to resting in the same plane with an angular sum = 352° and P2 is along the axis (Figure 1).

Tetrazene **3a** proved to be relatively stable up to 65 °C. Above 65 °C, slow decomposition was noted, which resulted in the formation of several new species by NMR, but no obvious formation of **1**. This complex was also stable to strong external reductants (KC_8), both alone and in combination with mild heating. Similar stability is noted with **3c**. Somewhat smaller mesityl-containing **3b** is more thermally unstable and decomposed when exposed to reductants, which led to H_2NAr, H_2NMes, and a host of unidentified products.

Upon exposure of THF solutions of **3a** to light, the clear bright orange solution darkens to brown (Figure 2). Extended exposure yields an opaque, dark green solution. ^{31}P NMR spectroscopy of the crude reaction mixture shows a combination of mostly starting material **3a** and $Ru(=NAr)_2(PMe_3)_2$ (**1**), with small amounts of $ArN=PMe_3$ and PMe_3. The bis(imide) **1** was observed in 25% yield *in situ*, and blue $Ru(=NAr)_2(PMe_3)_2$ (**1**) was obtain upon recrystallization. The crystallographic data, as well as ^1H and ^{31}P NMR spectroscopy, for the complex prepared using this photochemical route are in good agreement with the Wilkinson report of **1**.[1]

The yield of this reaction appears to be limited by the absorption properties of the product, which prevents the photochemical reaction from progressing to completion (see Figure S36 in the SI). The absorption properties of all three ruthenium(II) tetrazene species are quite similar. (See the Supplementary Information for more details.)

Photolysis of mesityl-containing **3b** resulted in rapid decomposition. Within 8 h, the transparent orange solution changed to a pale yellow. Removal of the solvent followed by examination of the crude residue by ^1H and ^{31}P NMR provided an intractable mixture in which H_2NMes was the only identifiable product.

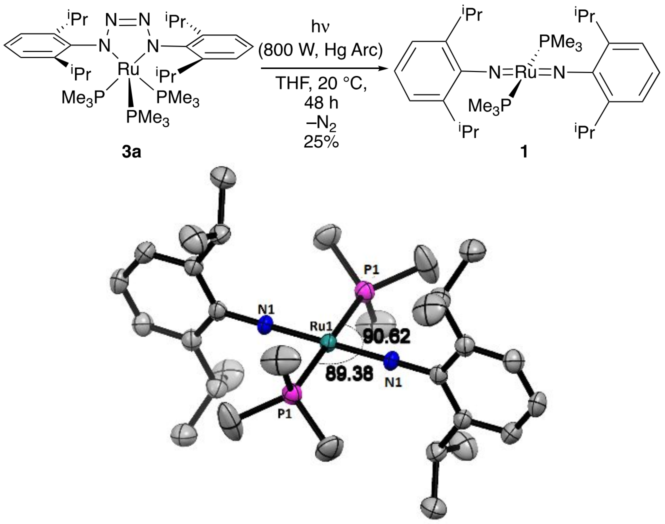
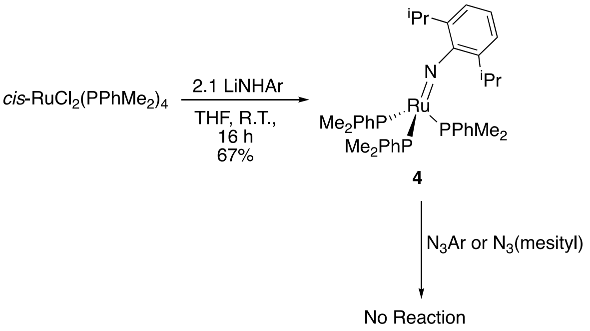


Figure 2. Photochemical conditions for the generation of $Ru(NAr)_2(PMe_3)_2$ via N_2 liberation from tetrazene **3a** and solid-state structure of $Ru(NAr)_2(PMe_3)_2$ (**1**) from X-ray diffraction. Ellipsoids are shown at the 50% probability level, and hydrogens in calculated positions are omitted for clarity. The Ru rests on a crystallographic inversion center.

Tetrazene Ru{N_4(Ar)Ar*}$(PMe_3)_3$ (**3c**) seems to undergo the same photochemical reaction as **3a** to give a square planar bis(imide) complex analogous to **1**. However, due to the enhanced solubility of both the product and the starting material relative to **3a**, Ru(=NAr)(=NAr*)$(PMe_3)_2$ could not be crystallized from the reaction mixture and fully characterized.

In an additional study, $PPhMe_2$ was used in place of PMe_3 in the initial synthesis (Scheme 2). The starting complex *cis*-$RuCl_2(PPhMe_2)_4$ was prepared, and reaction of this complex with LiNHAr provided the Ru(II) mono(imide) related to **2**, $Ru(NAr)(PPhMe_2)_3$ (**4**). However, the complex does not react with either ArN_3 or (mesityl)N_3.



Scheme 2. Synthesis of a terminal Ru(II) imide with bulkier phosphine ligands, $PPhMe_2$. Further reaction of $Ru(NAr)(PPhMe_2)_3$ with organic azides did not result in formation of a new product.

In contrast, using the larger $PPhMe_2$ phosphine with the smaller LiNH(mesityl) amide did not lead to the ruthenium imide complex, but instead (Figure 3) provided a C–H activation product Ru(κ_2(*N,C*)-1-(NH)-2-(CH_2)-4,6-$Me_2C_6H_2$)($PPhMe_2$)$_4$ (**5**). A similar reaction has been previously noted by Wilkinson and Hursthouse.[14] These observations perhaps point towards a very delicate steric balance between the phosphine and groups on the imide ligands that offers a limited window of stability for this class of complexes.

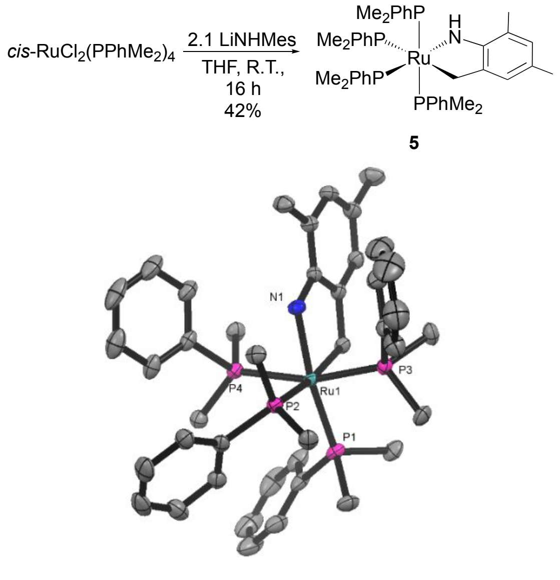


Figure 3. Synthesis of **5** and solid-state structure from X-ray diffraction shown with ellipsoids at 50% probability. Hydrogens in calculated positions and hexane from crystallization are omitted for clarity.

With the Ru(NAr)$_2$(PMe_3)$_2$ complex isolated via this photochemical synthesis, an *in situ* examination of the reactivity of this compound with alkynes was pursued. Based on ^1H and ^{14}N NMR, in comparison to the known Os derivative,[3] the Ru complex displays very similar reactivity toward alkynes. No reaction is observed upon addition of diphenylacetylene to Ru(NAr)$_2$(PMe_3)$_2$ in C_6D_6. Only upon addition of a phosphine scavenger, i.e. CuI (2 equiv), do the resonances for the PMe_3 ligands disappear and new chemical shifts for coordinated alkyne complex appear by ^1H and ^{14}N NMR. Previous studies of the Os(NAr)$_2$(η_2-diphenylacetylene) complex, and related Re(NAr)$_2$(NpC≡CNp), suggest that the metal coordinates to the alkyne π-system (Figure 4).[2, 3, 16] Based on similarities between the Os and Ru derivative, we suggest that the ruthenium binds similarly to the alkyne.

For comparison, we examined several known osmium species. The ^{14}N NMR chemical shifts for Os(NAr)$_2$(PMe_3)$_2$, Os(NAr)$_2$(η_2-diphenylacetylene), and Os(NAr)$_2$(O)$_2$ were observed at 283.0, 365.6, and 390.8 ppm, respectively. We can see a similar trend with the Ru values, where Ru(NAr)$_2$(PMe_3)$_2$ has a chemical shift at 303.3 ppm and Ru(NAr)$_2$(η_2-diphenylacetylene) at 387.1 ppm.[17]

In sum, we are able to find a new reliable route to Wilkinson's square planar, ruthenium(IV) complex Ru(NAr)$_2$(PMe_3)$_2$ through photochemical degradation of a tetrazene complex. The steric profile of the phosphine and imide ligands appear to be critical to isolation of this novel class of complexes.

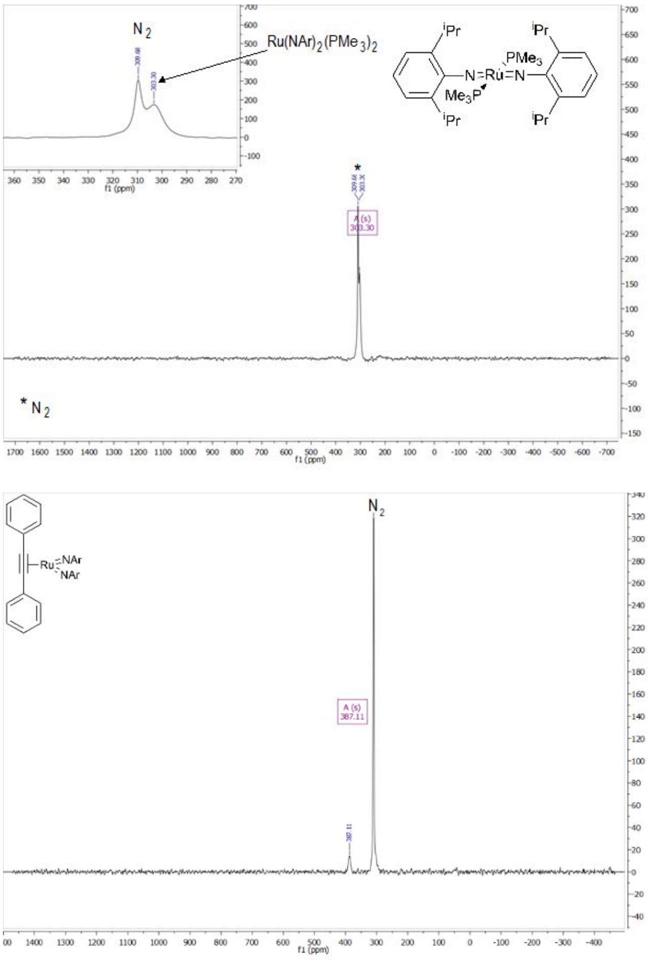


Figure 4. *top*) ^{14}N NMR spectrum of Ru(NAr)$_2$(PMe_3)$_2$ showing a resonance at 303 ppm. (*bottom*) ^{14}N NMR of Ru(NAr)$_2$(η_2-diphenylacetylene) showing a resonance at 387 ppm. Note, both spectra are referenced to dissolved N_2, which gives a very sharp resonance at 309.6 ppm, and liquid ammonia as 0 ppm.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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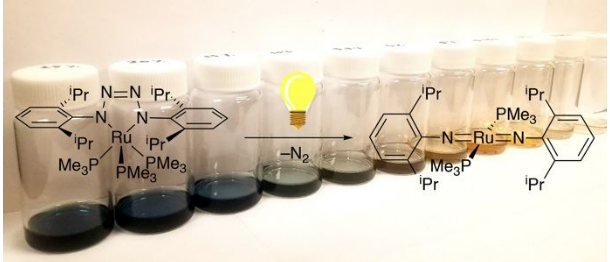
Notes and references

1. A. A. Danopoulos, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *Polyhedron*, 1992, **11**, 2961-2964.
2. M. H. Schofield, T. P. Kee, J. T. Anhaus, R. R. Schrock, K. H. Johnson and W. M. Davis, *Inorg. Chem.*, 1991, **30**, 3595-3604.
3. J. R. Wolf, G. C. Bazan and R. R. Schrock, *Inorg. Chem.*, 1993, **32**, 4155-4156.
4. A. K. Singh, B. G. Levine, R. J. Staples and A. L. Odom, *Chem. Commun.*, 2013, **49**, 10799-10801.

5. B. J. Coe and S. J. Glenwright, *Coord. Chem. Rev.*, 2000, **203**, 5-80.
6. K. E. F. Aldrich, B. S.; Singh, A. K.; Staples, R. J.; McCracken, J.; Levine, B.; Smith, M. R.; Odom, A. L. , *Inorg. Chem.*, 2019, submitted.
7. B. Hansert and H. Vahrenkamp, *J. Organometallic Chem.*, 1993, **459**, 265-269.
8. K.-M. Lin, P.-Y. Wang, Y.-J. Shieh, H.-Z. Chen, T.-S. Kuo and Y.-C. Tsai, *New J. Chem.*, 2010, **34**, 1737-1745.
9. T. Gehrmann, J. Lloret Fillol, H. Wadepohl and L. H. Gade, *Organometallics*, 2012, **31**, 4504-4515.
10. S. A. Cramer, R. Hernandez Sanchez, D. F. Brakhage and D. M. Jenkins, *Chem. Commun.*, 2014, **50**, 13967-13970.
11. C. Ni, J. C. Fettinger, G. J. Long, M. Brynda and P. P. Power, *Chem. Commun.*, 2008, DOI: 10.1039/B810941A, 6045-6047.
12. L. Wang, L. Hu, H. Zhang, H. Chen and L. Deng, *J. Am. Chem. Soc.*, 2015, **137**, 14196-14207.
13. A. A. Danopoulos, G. Wilkinson, T. K. N. Sweet and M. B. Hursthouse, *Dalton Trans.*, 1996, DOI: 10.1039/DT9960003771, 3771-3778.
14. A. A. Danopoulos, R. S. Hay-Motherwell, G. Wilkinson, S. M. Cafferkey, T. K. N. Sweet and M. B. Hursthouse, *Dalton Trans.*, 1997, DOI: 10.1039/A703028B, 3177-3184.
15. A. H. Obenhuber, T. L. Gianetti, X. Berrebi, R. G. Bergman and J. Arnold, *J. Am. Chem. Soc.*, 2014, **136**, 2994-2997.
16. D. S. Williams and R. R. Schrock, *Organometallics*, 1993, **12**, 1148-1160.
17. J. Mason, *Multinuclear NMR*, Plenum Press, New York, 1987.

Table of Contents Graphic



A square planar Ru(IV) bis(imide) can be synthesized by photolysis of a tetrazene starting material.