Towards Oligoclusters – Chemistry and Properties

Mark G. Humphrey

Department of Chemistry, Australian National University, Canberra, ACT 0200, Australia
E-mail: mark.humphrey@anu.edu.au

Summary: The recent progress of the author's research group in the syntheses, electronic properties and optical properties of monomeric and oligomeric organotransition metal cluster-containing systems is reviewed.

Keywords: cluster; electrochemistry; mixed-metal; oligomer; optical limiting

Introduction

A determined worldwide push has clarified several aspects of organotransition metal cluster chemistry - particularly well-established are synthetic methods to small homometallic clusters (those with three- or four-metal-atom cores), and aspects of their reaction chemistry.[1] Considerably less well-established, but of topical interest, are protocols to assemble clusters into oligocluster arrays and the physical properties of clusters (e.g. electronic, optical, magnetic, etc.). Significant interest has been shown recently in organotransition metal-containing polymers[2] and in metallodendrimers and metallostars,[3] metal-containing branched molecules whose molecular architectures offer prospects of a range of new applications. Thus far, however, few cluster-containing examples are extant. Some recent work has emphasized network structures based on the $Re_6(\mu_3\text{-}E)_8L_6$ core: see, for example, Ref. [4]. Cluster-containing oligomers are also relatively rare, despite the fact that such oligocluster arrays promise processable functional materials (note that many studies have examined the coordination of metal clusters to prefunctionalized polymers, mainly through *P*-linkages,[5-15] but also *via* *O*-[16] *C*-,[17-19] and *N*-interactions;[20] however, polymer supports of this type frequently result in polycoordination,[9] affording a mixture of mono- and poly-substituted clusters, together with non-coordinated polymer-bound ligands attached to the backbone). Only a few examples of oligomers with clusters in the oligomer backbone are extant.[21-24] Most cluster-containing polymers contain cluster units linked by *P*- or *N*-ligands or isocyanides, all of which can potentially be displaced

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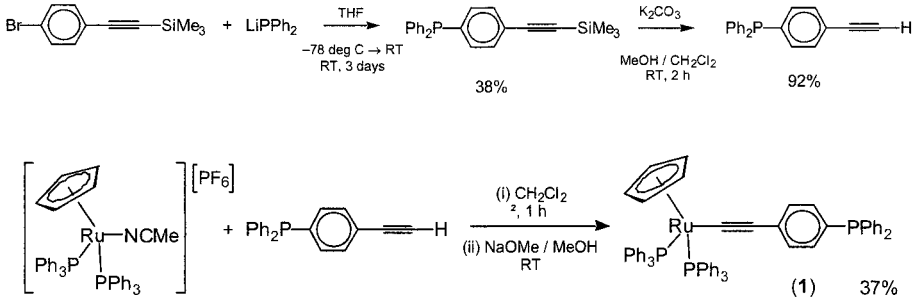
leading to polymer breakdown, and all examples except $\{Ru_6(\mu_6\text{-}C)(CO)_{15}(Ph_2PC_2PPh_2)\}_n$ are insoluble - new routes to soluble cluster-containing polymers are clearly required. Cluster-containing dendrimers and "star" molecules have also been the subject of very few reports,[25-27] although their metal-rich composition and electro-active nature may be useful in materials applications. In contrast, clusters linked through π-delocalizable backbones have come under considerable scrutiny, but the vast majority of such studies involve the linking of identical homometallic cores.[28-40] Introduction of a heterometal into the cluster core can further modify the electronic environment,[41] but very few examples of heterometallic clusters linked by unsaturated bridges exist.[42-44] Reported herein are our syntheses of a cluster-centered "star" molecule, cluster-containing oligourethanes, and mixed-metal oligo-cluster species in which the cluster units are linked by potentially π-delocalizable bridges.

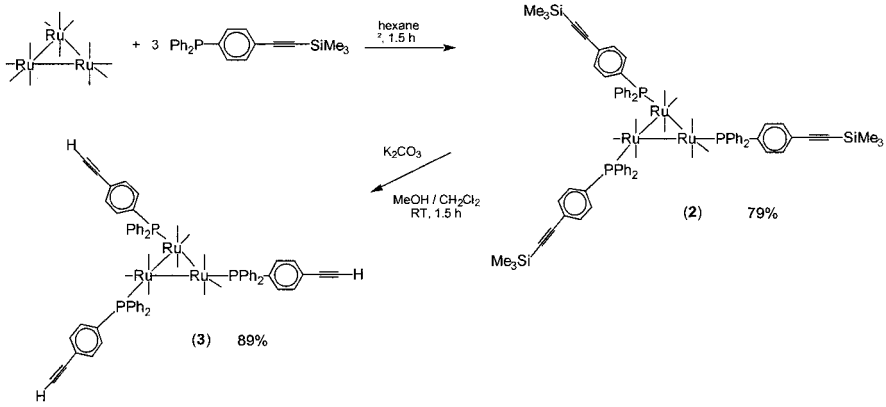
Optical limiters are materials that display decreasing transmittance as a function of incident light intensity (i.e. their optical transmission is power dependent). Efficient optical limiters are required for a range of applications in optical device protection - for example, such materials may be used for the protection of eyes and sensors from intense light pulses, as well as in laser mode locking and optical pulse shaping. Clusters (with fullerenes and phthalocyanines) have been identified as one of three promising classes of molecular optical limiters; all three can be viewed as reduced dimensionality materials with confined but potentially highly delocalizable electrons.[45] Optical limiting can arise from several phenomena (e.g. two-photon absorption (TPA), reverse saturable absorption (RSA)). The difference between the RSA process and TPA is that TPA is virtually instantaneous whereas processes involving an intermediate absorbing state exhibit certain kinetic behavior, which is dependent on the lifetimes of the states involved. Time-resolved investigations of the changes of absorptive properties are necessary to evaluate the mechanism of power limiting in a given system. The challenge at present is to develop an understanding of the underlying physical properties which give rise to the desired responses, and to design robust readily processable materials exhibiting optical limiting properties. Also summarized herein are our studies of the optical limiting behavior of systematically-varied mixed-metal clusters and a cluster-containing oligourethane.

Results and Discussion

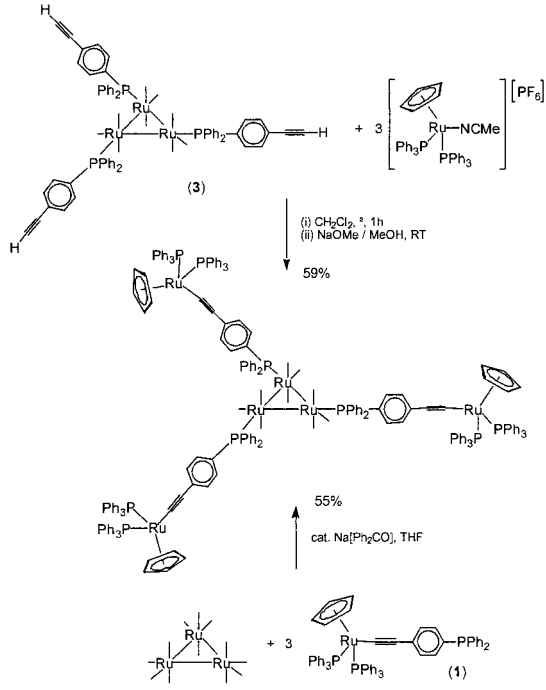
A cluster-centered "star". Dendrimers with clusters at the periphery are examples of nanoscale molecular architectures of considerable current interest,[46-48] but branched molecules with clusters at the core are little-explored. The well-established facile tris-substitution of $Ru_3(CO)_{12}$ by *P*-donor ligands suggests that it could function as a core unit and branching point in dendrimer construction and, indeed, that with the use of appropriate bifunctional ligands one can construct cluster-centered "star" molecules. With this in mind, we synthesized new phosphines bearing functional alkynyl units to facilitate dendrimer and star formation. The new phosphines $Ph_2PC_6H_4$-4-C≡CR [R = $SiMe_3$, H] were used to prepare $Ru(C{\equiv}CC_6H_4\text{-}4\text{-}PPh_2)(PPh_3)_2(\eta\text{-}C_5H_5)$ (**1**) (Scheme 1) and $Ru_3(CO)_9(Ph_2PC_6H_4\text{-}4\text{-}C{\equiv}CSiMe_3)_3$ (**2**) (Scheme 2), respectively, the former with a pendent phosphine. Reaction of **2** with carbonate or fluoride gave $Ru_3(CO)_9(Ph_2PC_6H_4\text{-}4\text{-}C{\equiv}CH)_3$ (**3**) with pendent terminal alkyne groups (Scheme 2). Reaction of **3** with $[Ru(NCMe)(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$ or reaction of $Ru_3(CO)_{12}$ with **1** afforded $Ru_3(CO)_9\{(Ph_2PC_6H_4\text{-}4\text{-}C{\equiv}C)Ru(PPh_3)_2(\eta\text{-}C_5H_5)\}_3$, a cluster-centered star (Scheme 3).[49]



Scheme 1. Synthesis of $Ru(C{\equiv}CC_6H_4\text{-}4\text{-}PPh_2)(PPh_3)_2(\eta\text{-}C_5H_5)$ (**1**).

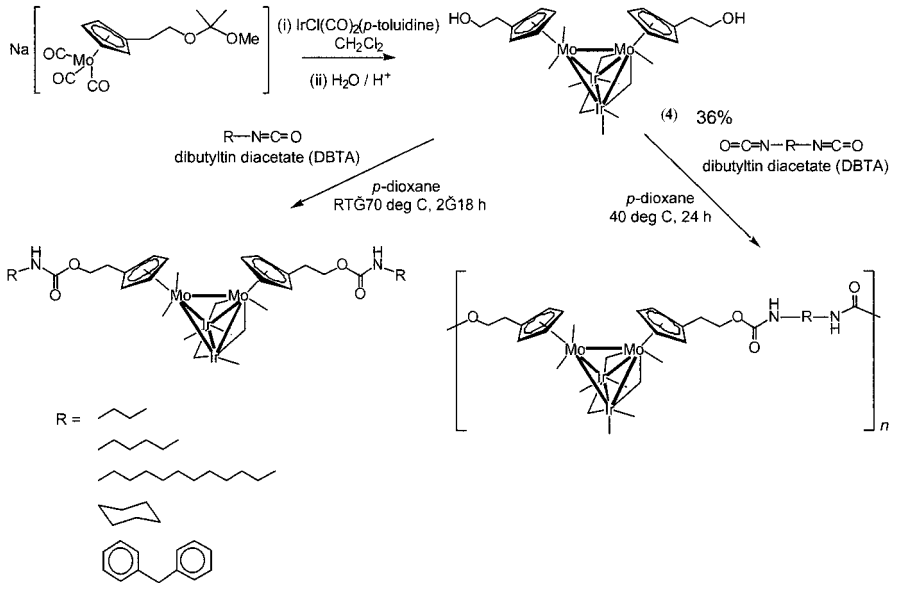


Scheme 2. Synthesis of $Ru_3(CO)_9(Ph_2PC_6H_4\text{-}4\text{-}C{\equiv}CSiMe_3)_3$ (**2**) and $Ru_3(CO)_9(Ph_2PC_6H_4\text{-}4\text{-}C{\equiv}CH)_3$ (**3**).



Scheme 3. Syntheses of $Ru_3(CO)_9\{(Ph_2PC_6H_4\text{-}4\text{-}C{\equiv}C)Ru(PPh_3)_2(\eta\text{-}C_5H_5)\}_3$.

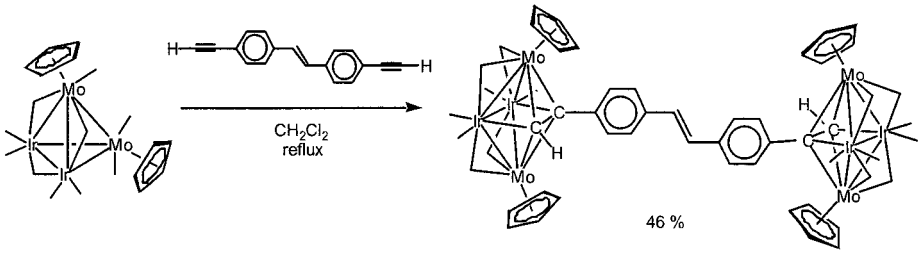
Cluster-containing oligourethanes. As was mentioned above, one particular problem with previously-reported cluster-containing polymers is the ease of polymer breakdown. Replacing the *P*- or *N*-ligands with substituted cyclopentadienyl ligands, which are significantly more strongly bound to clusters, should remedy this problem. Polyamides, polyurethanes and polyureas containing photodegradable $Mo_2(CO)_6(\eta\text{-}C_5H_4R)_2$ units along the polymer backbone have been reported previously.[50-56] We replaced the photo-active $Mo_2(CO)_6(\eta\text{-}C_5H_4R)_2$ groups in these polymers with photo-stable cluster units, affording the first cluster-containing oligomers in which the clusters are in the structurally-uniform environment of the oligomer backbone and attached via robust cyclopentadienyl groups.[57] Bis(hydroxyalkylcyclopentadienyl)-containing mixed molybdenum-iridium clusters $Mo_2Ir_2(CO)_{10}\{\eta\text{-}C_5H_4(CH_2)_xOH\}_2$ [x = 2 (**4**), 10] were reacted with alkyl or aryl 1,ω-diisocyanates OCNRNCO [R = $(CH_2)_y$ (y = 4, 6, 12), *trans*-1,4-cyclohexyl, or 4-$C_6H_4CH_2$-4-C_6H_4] to form oligourethanes with transition metal clusters in the oligomer backbone (Scheme 4; 46-89% yields).



Scheme 4. Preparation of oligourethanes containing clusters in the backbone and model compounds.

Characterization of the cluster-containing oligourethanes was aided by spectral comparison with model cluster-diurethanes $Mo_2Ir_2(CO)_{10}\{\eta\text{-}C_5H_4(CH_2)_2OC(O)NHRH\}_2$ [R = $(CH_2)_y$ [y = 4, 6, 12], *trans*-1,4-cyclohexyl; 37-72% yields] prepared from reaction between the cluster diol **4** and alkyl isocyanates HRNCO (Scheme 4). The extent of polymerization was assessed by gel permeation chromatography, with little dependence on diisocyanate precursor linker R, but strong dependence on alkylcyclopentadienyl linker length $(CH_2)_x$, suggesting that the steric influence of the bulky dimolybdenum-diiridium cluster core and co-ligands is the most important factor governing extent of polymerization.

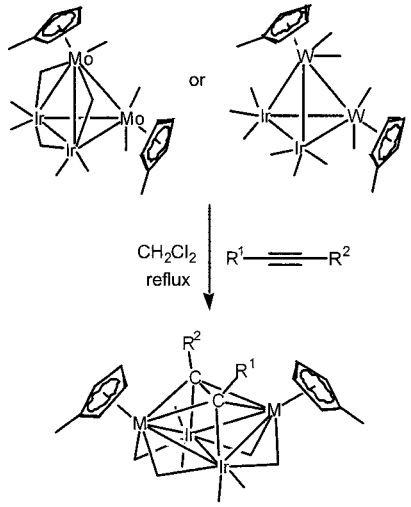
π-Delocalizable bridge-linked clusters. Following these studies of cluster-containing oligourethanes, in which the cluster units are linked via saturated bridges, our attention was drawn to the possibility of linking such clusters by unsaturated bridging groups, initial studies focussing on di- and tri-cluster units linked by a variety of potentially π-delocalizable bridges (phenylene, phenylenevinylene, phenyleneethynylene, thienyl, selenienyl); ligation of the π-bridge to the cluster core was by a μ_4-η^2-bound alkyne, a particularly robust interaction. Our first attempt employed a cyclopentadienyl-containing cluster and a di-terminal alkyne (Scheme 5), but the limited solubility of the product complicated purification, so subsequent studies utilized methylcyclopentadienyl-containing clusters and n-hexyl-containing internal alkynes, dramatically enhancing solubility.[58]



Scheme 5. Preparation of a *trans*-stilbene linked dicluster compound.

Alkynes react with these tetrahedral dimolybdenum-diiridium or ditungsten-diiridium clusters by formal insertion of the C_2 unit into the Mo-Mo or W-W bond to afford robust clusters with pseudooctahedral core geometries. Because we were interested in examining the modification of

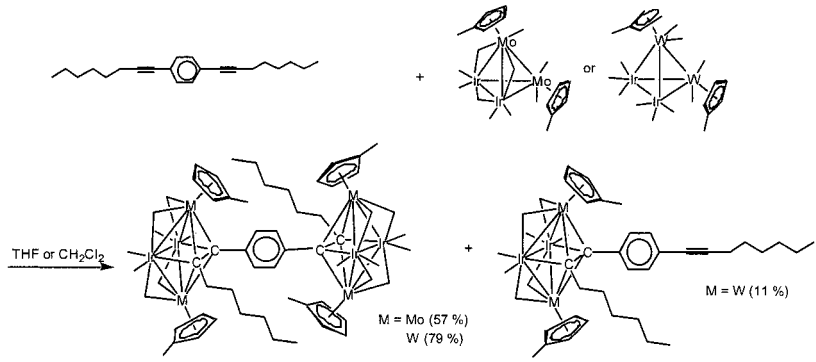
properties upon linking clusters by π-delocalizable bridges, we prepared several mono-cluster model compounds to benchmark an isolated cluster unit, together with mono-cluster compounds with functionalized alkynes suitable for coupling to form di-cluster compounds (Scheme 6).[58]



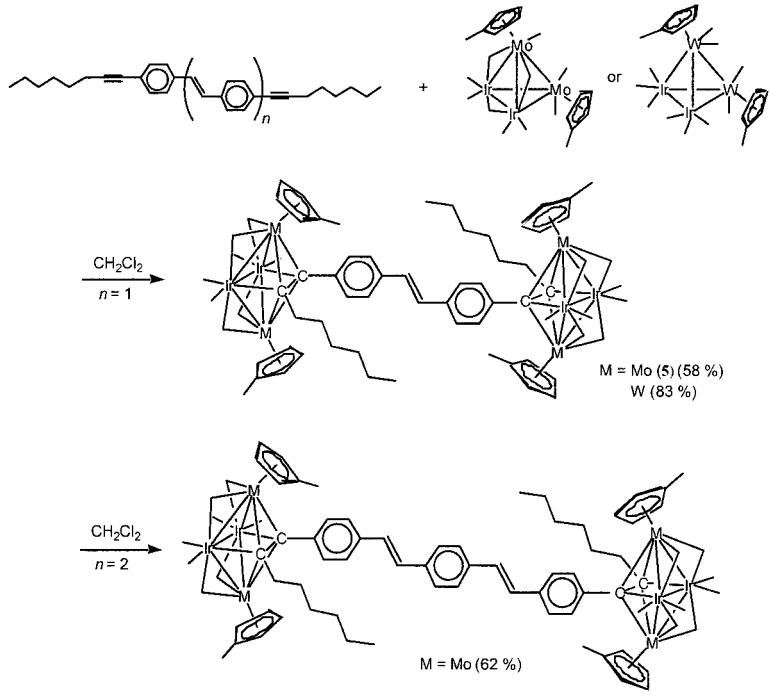
	M	R^1	R^2	Yield (%)
	Mo	H	Ph	46
	Mo	Ph	Ph	81
	Mo	Me	Ph	50
	W	Me	Ph	79
6	Mo	*n*-hexyl	C_6H_4-4-CHO	59
7	Mo	*n*-hexyl	C_6H_4-4-$CH_2P(O)(OEt)_2$	66

Scheme 6. Syntheses of mono-cluster compounds.

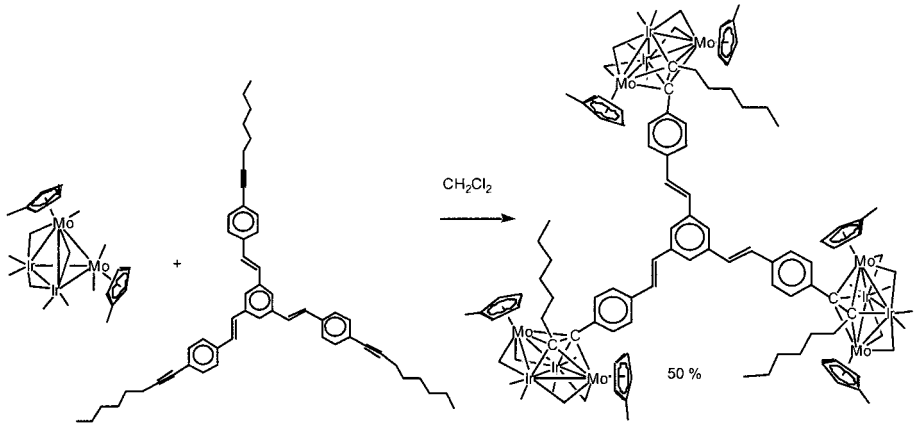
Similar reactions between tetrahedral cluster precursors and vinylene-linked di- or tri-ynes afforded related di- or tri-cluster compounds in which two or three cluster units are linked by unsaturated bridges (Schemes 7-9).[58]



Scheme 7. Syntheses of phenylene-linked di-cluster compounds.

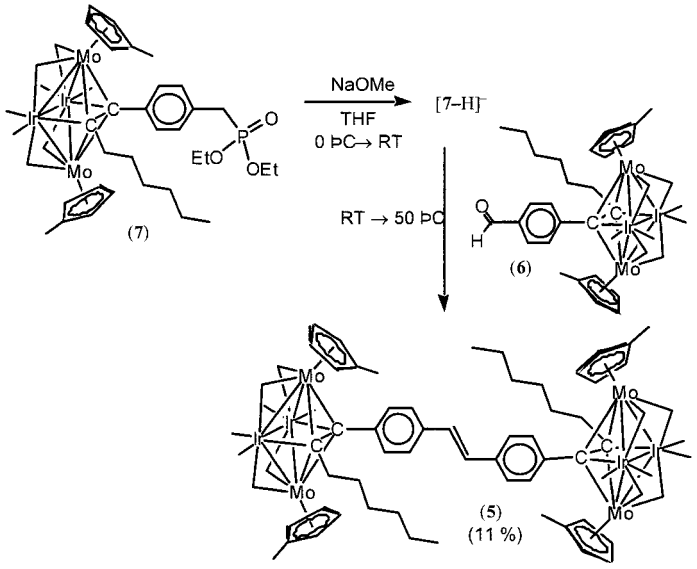


Scheme 8. Syntheses of phenylenevinylene-linked di-cluster compounds.



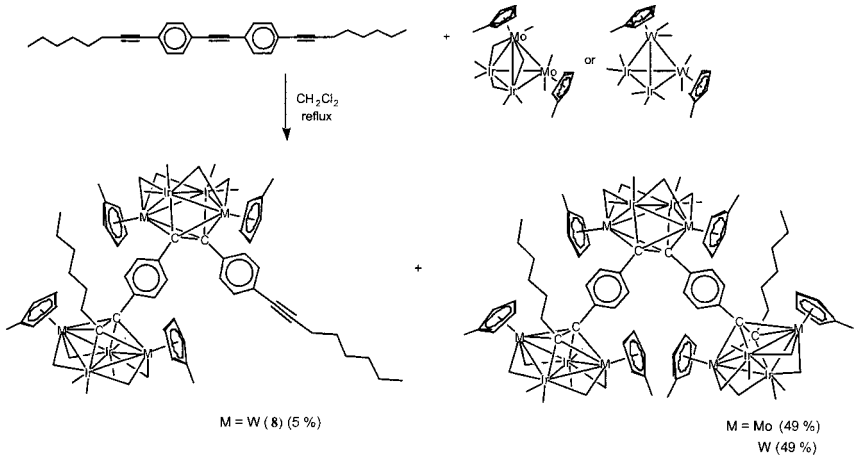
Scheme 9. Synthesis of a phenylenevinylene-linked tri-cluster compound.

Compound **5** was also prepared by coupling **6** and **7** under Emmons-Horner conditions, but in a lower yield (Scheme 10).[58]

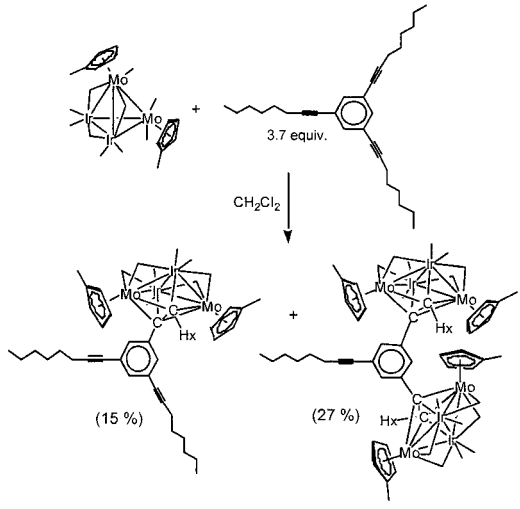


Scheme 10. Synthesis of a di-cluster compound by Emmons-Horner coupling.

Reactions between the tetrahedral mixed-metal clusters and ethynylene-linked di- or triynes afforded related mono-, di- or tri-cluster compounds (Schemes 11 and 12). Attempts to add a third cluster to the 1,3,5-tris(1-octynyl)benzene were unsuccessful, presumably due to steric reasons.[59]

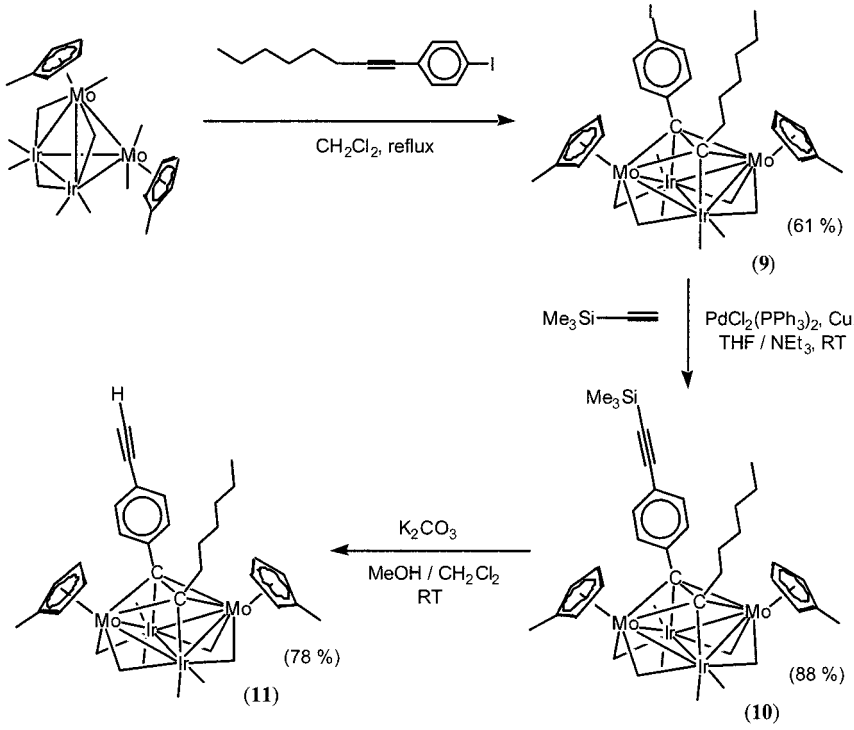


Scheme 11. Synthesis of phenyleneethynylene-linked di- and tri-cluster compounds.



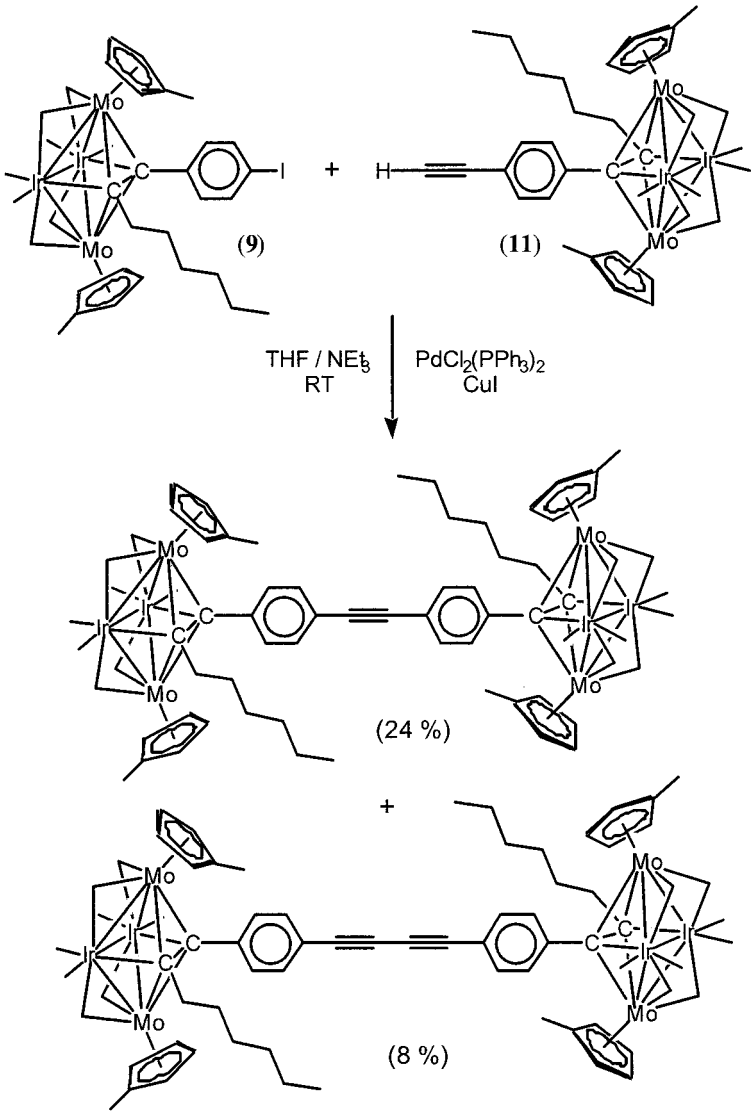
Scheme 12. Synthesis of 1,3,5-tris(1-octynyl)benzene mono- and di-cluster compounds.

Compound **8** corresponds to the 1,2-dicluster adduct of the linear triyne $Me(CH_2)_5C{\equiv}C\text{-}4\text{-}C_6H_4C{\equiv}C\text{-}4\text{-}C_6H_4C{\equiv}C(CH_2)_5Me$. No 1,3-dicluster isomer was isolated from direct reaction, but the related molybdenum-containing 1,3-dicluster isomer was prepared by exploiting organic reaction chemistry on pre-coordinated functionalized alkyne ligands (Schemes 13 and 14).



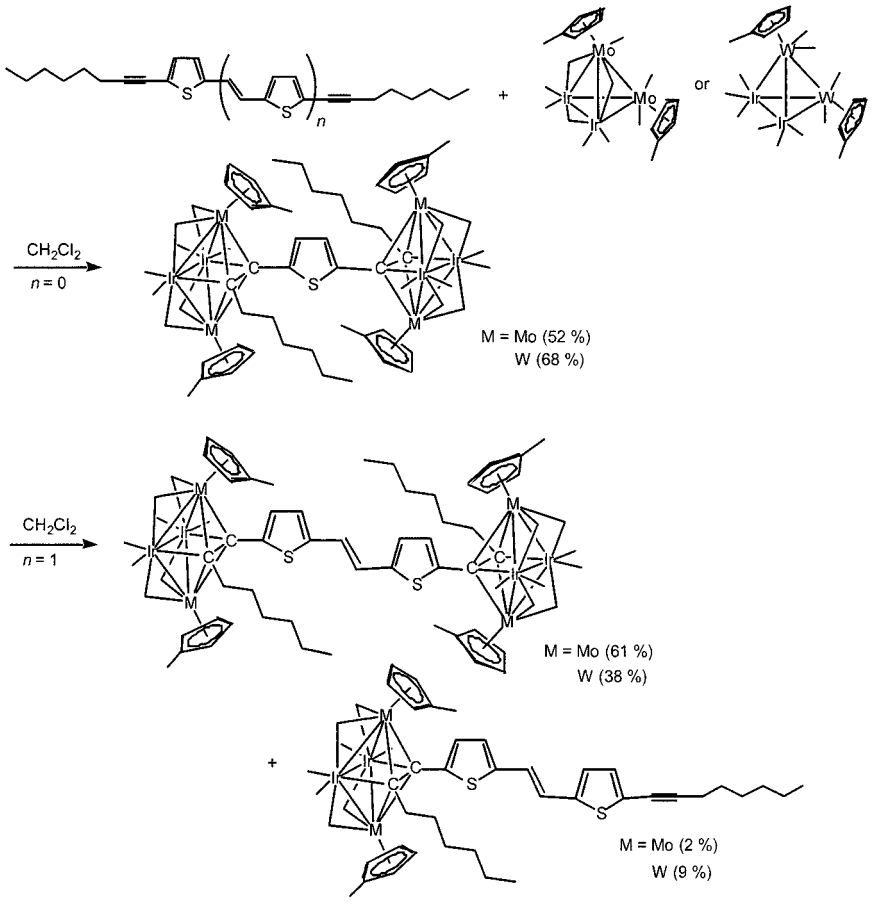
Scheme 13. Synthesis of pendent alkyne-containing mixed-metal clusters.

Sonogashira coupling of **9** with $Me_3SiC{\equiv}CH$ and subsequent desilylation afforded $Mo_2Ir_2\{\mu_4\text{-}\eta^2\text{-}Me(CH_2)_5C_2\text{-}4\text{-}C_6H_4C{\equiv}CR\}(CO)_8(\eta^5\text{-}C_5H_4Me)_2$ [R = $SiMe_3$ (**10**), H (**11**)]. Sonogashira coupling of **9** and **11** gave the 1,3-isomer $[Mo_2Ir_2(CO)_8(\eta^5\text{-}C_5H_4Me)_2]_2\{\mu_8\text{-}\eta^4\text{-}Me(CH_2)_5C_2\text{-}4\text{-}C_6H_4C{\equiv}CC_6H_4\text{-}4\text{-}C_2(CH_2)_5Me\}$, as well as the homo-coupling product.[59]

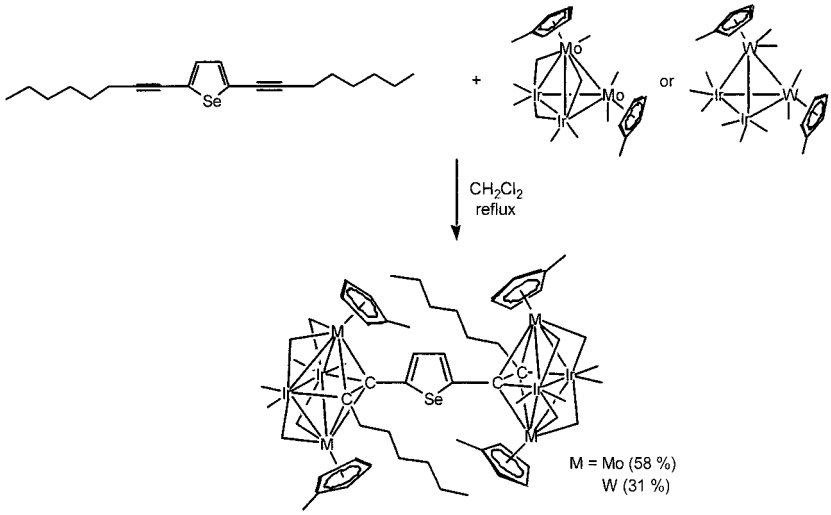


Scheme 14. Synthesis of a 1,3-dicluster isomer and homocoupled product.

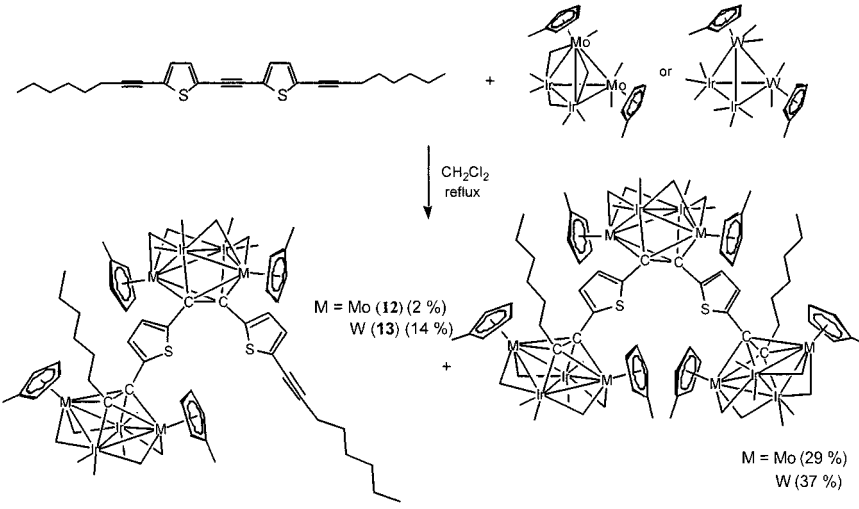
Compounds with heterocycle-containing bridges are accessible by similar procedures. The tetrahedral mixed-metal clusters reacted with heterocyclic di- or triynes to afford the analogous mono-, di- or tri-cluster compounds to the phenyl-containing examples above (Schemes 15-17).[60]



Scheme 15. Syntheses of thienyl-linked di-cluster compounds.

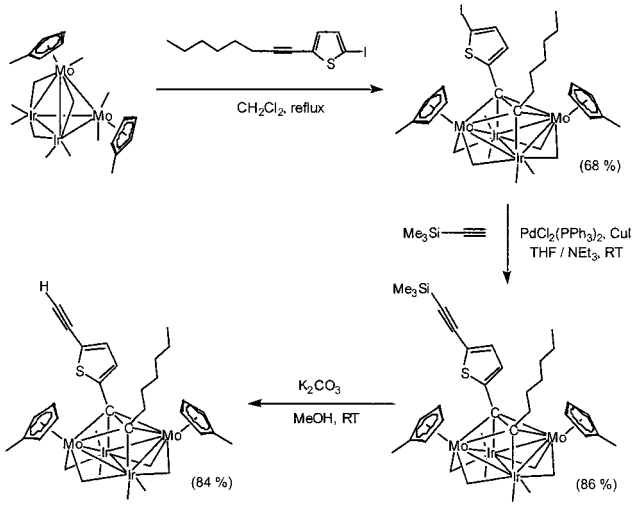


Scheme 16. Synthesis of selenienyl-linked di-cluster compounds.

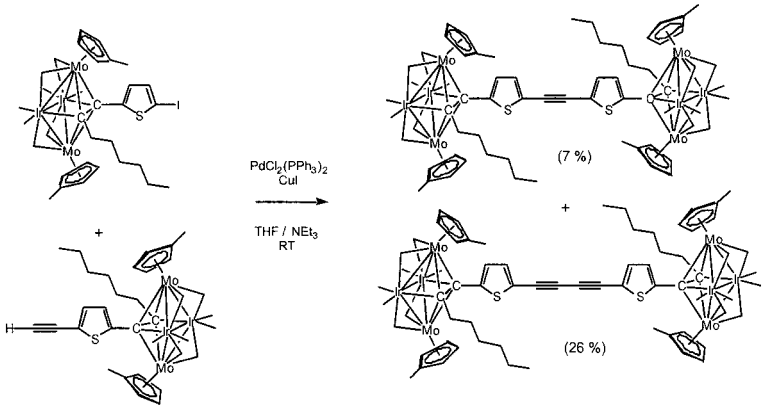


Scheme 17. Syntheses of thienylethynylene-linked di- and tri-cluster compounds.

Compounds **12** and **13** correspond to the 1,2-dicluster adducts of the linear triyne $Me(CH_2)_5C{\equiv}C\text{-}5\text{-}C_4H_2S\text{-}2\text{-}C{\equiv}C\text{-}2\text{-}C_4H_2S\text{-}5\text{-}C{\equiv}C(CH_2)_5Me$. As with the analogous phenyl-based chemistry, no 1,3-dicluster isomer was isolated from direct reaction, but the molybdenum-containing 1,3-dicluster isomer was prepared by exploiting organic reaction chemistry on pre-coordinated functionalized alkyne ligands (Schemes 18 and 19).[60]

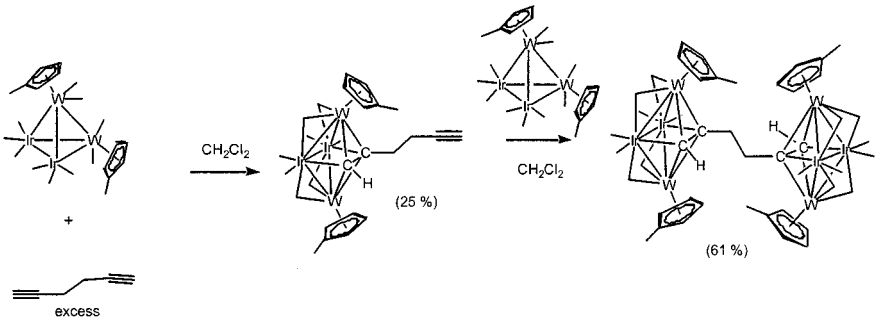


Scheme 18. Synthesis of pendent alkyne-containing mixed-metal clusters.



Scheme 19. Synthesis of a 1,3-dicluster isomer and homocoupled product.

A di-cluster compound with a saturated bridge was prepared in a similar manner (Scheme 20).[58]



Scheme 20. Synthesis of a di-cluster compound with a saturated bridging group.

The properties of these systematically-varied oligo-cluster compounds are currently being studied. Cyclic voltammetric scans for many examples have been collected. All compounds show a reversible/partially-reversible oxidation, followed by an irreversible oxidation process; potentials for the former increase on replacement of tungsten by molybdenum and alkyne substituent variation Me < H < Ph. UV-vis-NIR spectroelectrochemical studies of the first oxidation process show similar spectral progressions for mono- and di-cluster compounds. The reductive cyclic voltammetric scans for compounds in which clusters are linked by long unsaturated bridges show one irreversible reduction process, whereas compounds in which *n* cluster cores are linked by a phenylene unit show *n* irreversible reduction processes. Density functional calculations indicate that oxidation and reduction both proceed with retention of the pseudooctahedral core geometry, but that loss of a carbonyl ligand concomitant with two-electron reduction is energetically accessible, suggesting that this accounts for the irreversibility of the reduction step.[58-60]

Optical limiting properties of clusters. Metal carbonyl clusters tend to be obtained as crystalline materials rather than in a film-processable form required for putative optical applications. However, access to oligomers and polymers with clusters in the backbone should afford processable cluster-containing materials where the clusters are in the uniform chemical environments required to standardize molecular optical properties. We have commenced a study

of the optical limiting behavior of our mixed-metal clusters; this has involved development of preliminary structure-activity trends, and examination of the temporal nature of the optical limiting response in this class of optical limiter.[61]

Linear optical absorption spectra were obtained. Progression from tetrahedral molybdenum-triiridium cluster to dimolybdenum-diiridium cluster and replacing molybdenum by tungsten both shift the optical absorption maxima to lower energy. All clusters contain broad low intensity absorptions through the visible region, suggestive of potential as broad-band optical limiters. Incorporation of the cluster into the polymer does not result in modification of the optical spectrum, consistent with electronically "insulated" clusters, as expected, permitting optical properties of the cluster to be exploited while processability is enhanced.

The optical limiting properties were assessed by open-aperture Z-scan (ns pulses, 523 nm) and time-resolved pump-probe studies (ps pulses, 527 nm). A typical data set and ideal fitted curve from the former is shown in Figure 1.

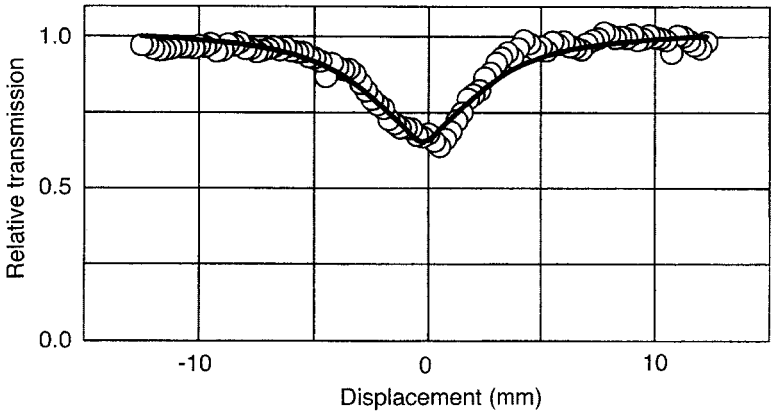
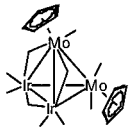
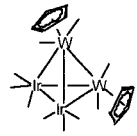
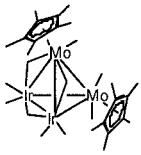
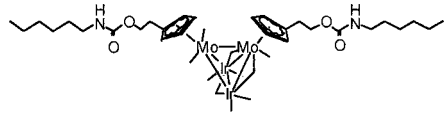
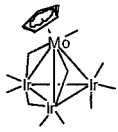
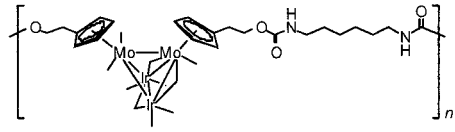


Figure 1. Z-scan data set and ideal fitted curve for $Mo_2Ir_2(CO)_{10}(\eta\text{-}C_5Me_5)_2$.

We have utilized the effective nonlinear absorption coefficient, β_2, which is extracted from the curve and extrapolated to pure substance, as an indicator of optical limiting potential. Results from tetrahedral mixed group 6 - iridium clusters are displayed in Table 1.

Table 1. Optical limiting results from open aperture Z-scan experiments

	β_2 (10^{-6} cm /W)[a]		β_2 (10^{-6} cm/W)[a]
	56		74
	42		38
	24		48

[a] ± 20 %

Several trends in β_2 are revealed by this study (while being mindful of the error margins). The molybdenum-triiridium cluster exhibited a lower nonlinear absorption coefficient than its dimolybdenum-diiridium cluster analogue. Alkylation of the cyclopentadienyl ring also decreased this coefficient, although less significantly so. Replacing tungsten by molybdenum resulted in a decrease in β_2. The incorporation of the clusters into polymers increases processability, but does not appear to diminish nonlinear absorption, consistent with the optical limiting response originating from the ligated metal core, and with no inter-cluster electronic interaction to influence optical limiting.

Employing nanosecond laser pulses to measure nonlinear absorption can result in many time-dependent photophysical processes becoming integrated into the response. We therefore employed a time-resolved pump-probe experiment, from which one can derive excited state lifetimes (τ) and absorption cross sections ('ease of absorption' between two states, σ). The results from a 527 nm pump-probe experiment (pulses ca 50 ps, pump fluence at the sample *ca*

1 J cm^{-2}) on a solution of $Mo_2Ir_2(\mu_4\text{-}\eta^2\text{-}MeC_2Ph)(CO)_8(\eta\text{-}C_5H_4Me)_2$ are shown in Figure 2.

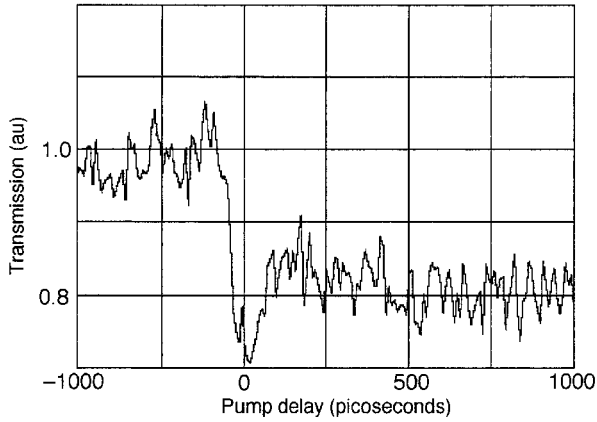


Figure 2. Results from a 527 nm ps pump-probe experiment on $Mo_2Ir_2(\mu_4\text{-}\eta^2\text{-}MeC_2Ph)(CO)_8(\eta\text{-}C_5H_4Me)_2$.

The negative peak at 0 ps is likely to arise from an instantaneous TPA phenomenon when the probe beam arrives simultaneously with the pump beam. When the probe beam arrives after the pump beam, a long-lived tail is observed (transmission ≈ 0.8), likely to result from excited state absorption and the formation of metastable states; the lower energy excited states (metastable states) are sufficiently populated by the intense pump beam that absorption of photons from the probe beam (to higher energy excited states) becomes possible, resulting in a lower transmission. Figure 2 shows that the metastable states, required for the excited state absorption, are long-lived (> 1000 ps). The alkyne-adduct $Mo_2Ir_2(\mu_4\text{-}\eta^2\text{-}MeC_2Ph)(CO)_8(\eta\text{-}C_5H_4Me)_2$ can thus be classed as an optical power limiter exhibiting both TPA and RSA.

Conclusions

The studies summarized herein have demonstrated the facile synthesis of a variety of di-, tri- and oligo-cluster compounds of linear and branched geometries and with saturated and unsaturated bridging groups. Structure-optical limiting behavior relationships for the tetrahedral core mixed-metal clusters were developed. A time-resolved investigation of the alkyne-adduct $Mo_2Ir_2(\mu_4\text{-}\eta^2\text{-}$

$MeC_2Ph)(CO)_8(\eta\text{-}C_5H_4Me)_2$ using ps pulses at 527 nm revealed optical power limiting behavior resulting from electronic processes [a fast nonlinear absorption process followed by reverse saturable absorption involving long-lived (>1000 ps) metastable excited states].

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