

### Preliminary communication

## Trindenyl[tris(rheniumtricarbonyl)]

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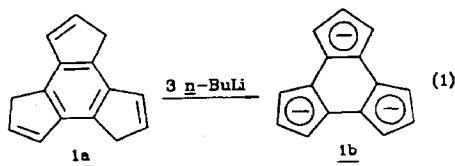
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### Abstract

Trindene is combined with KH and  $[\text{Re}(\text{CO})_3(\text{THF})\text{Br}]_2$  (THF = tetrahydrofuran) in THF to yield the first trinuclear half-sandwich complex of the trindene trianion, (trindenyl) $[\text{Re}(\text{CO})_3]_3$ , in 50% yield. Two of the rhenium carbonyl units are rigidly held in close proximity and the carbonyl ligands on adjacent metals are vibrationally coupled. Both *cis* and *trans* isomers of the dirhenium complex, (trindenyl) $[\text{Re}(\text{CO})_3]_2$ , are also isolated from the above reaction in low yield.

Intramolecular metal–metal cooperativity is being explored in complexes where metal atoms are held in close proximity in anticipation that unique chemical reactivity will result. Carbocyclic ligands that have been used to restrain metals for this purpose are fulvalene [1], indacene [2] and poly(cyclopentadienyl) ligands linked by either methylene [3] or methylsilyl [4] groups.

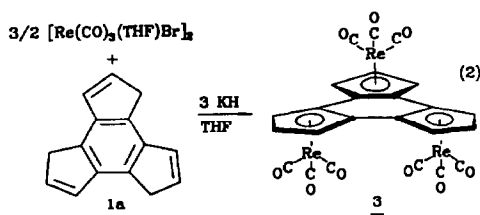
Katz and Slusarek [5] pioneered the synthesis of trindene, **1a**, which can be deprotonated with three equivalents of base to form the trianion, **1b**, (reaction 1).



The trindene trianion can be viewed as three fused cyclopentadienyl rings. We wished to explore the propensity of the trindene trianion to form polymetallic half-sandwich complexes which would provide a new and diverse group of substances with which to study the reactivity of metals in close proximity. Here we communicate the preparation of the *cis* and *trans* isomers of dirhenium-trindene complex, **2-cis** and **2-trans**, and the robust trirhenium carbonyl derivative of the trindene trianion, **3**.

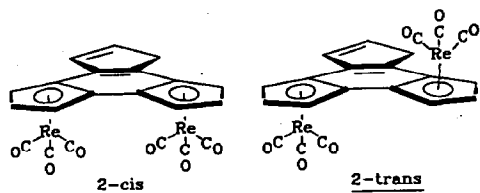
Trindene (0.26 mmol),  $[\text{Re}(\text{CO})_3(\text{THF})\text{Br}]_2$  [6] (0.39 mmol) and KH (0.90 mmol) are combined and stirred in 6 ml of THF for 12 h under dry, oxygen-free conditions

(reaction 2). The reaction mixture is stirred with excess  $\text{NH}_4\text{Cl}$  for 10 min.



Since KH does not react directly with  $[\text{Re}(\text{CO})_3(\text{THF})\text{Br}]_2$  but deprotonates trindenyl rapidly at room temperature, these three reagents can be combined at once. The reaction mixture is filtered, solvent is removed from the filtrate and the white residue is washed with  $\text{CH}_2\text{Cl}_2$ . The crude product is recrystallized from THF by evaporation and again washed with  $\text{CH}_2\text{Cl}_2$ . This yields 124 mg (48%, 0.120 mmol) of **3**.

Preparative TLC of the combined  $\text{CH}_2\text{Cl}_2$  extracts with 1 : 3 ethylacetate : hexane yields three fractions. These are recovered in the following order of decreasing mobility: **2-trans** (9 mg, 0.013 mmol, 5%), **3** (6 mg, 0.006 mmol, 2%) and **2-cis** (5 mg, 0.007 mmol, 3%). Spectroscopic data is collected in Table 1.



The products, **2-cis**, **2-trans** and **3** are all air stable as solids and in solution. This contrasts with the air-sensitive ligand precursor, trindenyl. Compound **3** exhibits exceptional thermal stability: It remained a white crystalline powder under vacuum to  $> 270^\circ\text{C}$ . The rigid trindenyl framework forces both **2-cis** and **3** to have two

Table 1

Spectral data for rhenium carbonyl complexes of the trindenyl trianion

Compound	IR <sup>a</sup> (rel. abs)	<sup>1</sup> H NMR <sup>b</sup>
<b>2-cis</b>	2030 (0.8), 2016 (0.3), 1946 (0.8), 1919 (1.0)	6.88 <sup>c</sup> (td, 1H, <i>J</i> 1.4, 5.3), 6.74 (td, 1H, <i>J</i> 1.4, 5.5), 6.26 (dd, 1H, <i>J</i> 1.4, 2.9), 6.16 (dd, 1H, <i>J</i> 1.4, 2.9), 5.71 (dd, 1H, <i>J</i> 1.4, 2.8), 5.58 (dd, 1H, <i>J</i> 1.4, 2.7), 5.38 (t, 1H, <i>J</i> 2.9), 5.34 (t, 1H, <i>J</i> 2.9), 3.54 (m, 2H)
<b>2-trans</b>	2017 (0.6), 1927 (1.0)	6.90 <sup>c</sup> (td, 1H, <i>J</i> 1.6, 5.5), 6.71 (td, 1H, <i>J</i> 1.5, 5.5), 5.86 (dd, 1H, <i>J</i> 1.5, 2.9), 5.83 (dd, H, <i>J</i> 1.4, 2.8), 5.82 (dd, 1H, <i>J</i> 1.4, 2.8), 5.72 (dd, 1H, <i>J</i> 1.5, 2.8), 5.64 (t, 1H, <i>J</i> 3.0), 5.63 (t, 1H, <i>J</i> 3.0), 3.53 (td, 1H, <i>J</i> 1.5, 24.0), 3.46 (td, 1H, <i>J</i> 1.5, 24.0)
<b>3</b> <sup>d</sup>	2034 (0.3), 2022 (0.9), 1949 (0.6) 1931 (1.0)	6.47 <sup>e</sup> (dd, 2H, <i>J</i> 1.4, 2.9), 6.12 (d, 2H, <i>J</i> 2.9), 5.99 (dd, 2H, <i>J</i> 1.4, 2.9), 5.90 (t, 1H, <i>J</i> 2.8), 5.55 (t, 2H, <i>J</i> 2.9)

<sup>a</sup> ( $\text{cm}^{-1}$ ,  $\nu(\text{CO})$ , THF). <sup>b</sup>  $\delta$ (1H, 300 MHz) downfield relative to TMS. <sup>c</sup>  $\text{CDCl}_3$  solvent. <sup>d</sup>  $^{13}\text{C}$  NMR, **3**, 194.4(s), 99.3(s), 98.9(s), 97.3(s), 89.0(d, *J* 184), 84.5(d, *J* 186), 83.2(d, *J* 184), 77.7(d, *J* 187), 77.0(d, *J* 185). Anal. Found: C, 29.21; H, 1.01.  $\text{C}_{24}\text{H}_9\text{O}_9\text{Re}_3$  calcd.: C, 28.83; H, 0.91%. <sup>e</sup> THF-*d*<sub>8</sub> solvent.

Re(CO)<sub>3</sub> groups juxtaposed. Their IR carbonyl stretching frequencies are vibrationally coupled while this coupling is absent for *2-trans* [2] (Table 1).

The reactivity of the trindene trianion parallels that of cyclopentadienide for the synthesis of rhenium tricarbonyl derivatives [7]. This suggests that a broad class of trindene metal complexes and combinations thereof can be studied under the unusual conditions of tightly packed metal sites. Identifying the unique chemical and physical properties which may result from these rigidly held adjacent metals is the focus of our continuing studies.

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