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# Spontaneous Formation of an Organometallic−Inorganic Dirhenium Carbonyl Cryptate Encapsulating a Sodium Cation

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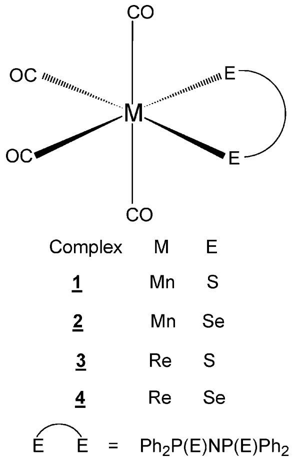
*Summary: The reactions between the rhenium(I) complexes [ReBr(CO)$_5$], [Re$_2$Br$_2$(CO)$_6$(THF)$_2$], and [ReOTf(CO)$_5$] and Na[Ph$_2$P(O)NP(O)Ph$_2$] in toluene and THF under reflux and in dichloromethane at room temperature, respectively, afforded the complex Na[Re$_2$(CO)$_6${$\mu$-Ph$_2$P(O)NP(O)Ph$_2$-$\kappa^2O$}$_3$] in good to medium yields; an X-ray crystallographic study in the solid state revealed that the sodium atom is enclosed in the cage formed by two −Re(CO)$_3$ fragments joined by three end-bound [Ph$_2$P(O)NP(O)Ph$_2$] ligands.*

The chemistry of the tetraphenyldichalcogenoimidodiphosphinate anions [Ph$_2$P(E)NP(E)Ph$_2$]$^-$ (E = O, S, Se) has been intensely studied over the past decade. Although their syntheses date back to the 1960s (for E = O,[1] S[2]) and late 1970s (for E = Se[3]), it was in the 1990s that most of their coordination chemistry, with both transition and main-group elements, was explored, as evidenced by the large numbers of reports on complexes containing these ligands.[4] The ability of the [Ph$_2$P(E)NP(E)Ph$_2$]$^-$ anions (E = O, S, Se) to ligate in different fashions and conformations is one of the reasons these ligands have been extensively studied; their potential applications to photonic devices and sensors,[5] biological activity,[6] and, recently, potential biomolecule labels in luminescent bioassays or materials for laser systems[7] (due to some imidodiphosphinate, [Ph$_2$P(O)NP(O)Ph$_2$]$^-$, complexes with long-lived near-infrared luminescent properties) have further contributed to the increasing interest in compounds containing these inorganic ligands. In an attempt to extend the coordination studies of anions of the type [R$_2$P(E)NP(E)R$_2$] (R = Ph, Me and E = O, S, Se) to low-valent transition metals, we turned our attention to the metal carbonyls of group 7. We found out that the sulfur anion [Ph$_2$P(S)NP(S)Ph$_2$]$^-$ coordinates in a $\kappa^2S$ fashion to the fragments M(CO)$_4$ to give complexes **1** (M = Mn)[8] and **3**[17] (M = Re) (Chart 1).

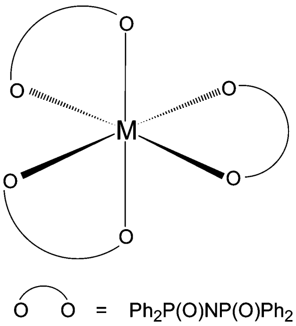
**Chart 1**



| Complex | M | E |
|---|---|---|
| **1** | Mn | S |
| **2** | Mn | Se |
| **3** | Re | S |
| **4** | Re | Se |

E E = Ph$_2$P(E)NP(E)Ph$_2$

**Chart 2**



O O = Ph$_2$P(O)NP(O)Ph$_2$

Complex **5**

This same coordination pattern is shared by the Se analogue [Ph$_2$P(Se)NP(Se)Ph$_2$]$^-$ with the Mn and Re bromo carbonyls (Chart 1; complexes **2** and **4**, respectively).[9] Interestingly, when Na[Ph$_2$P(O)NP(O)Ph$_2$] reacts with [MnBr(CO)$_5$] the Mn(III) complex **5** (Chart 2) is obtained by aerial oxidation;[10] a more detailed study shed light on the oxidation path whereby the Mn(III) complex is obtained, starting from the Mn(I) complex (the oxygen analogue of **1**−**4**) through a partial oxidation rendering a mixed-valence (Mn(II)−Mn(I)) dinuclear complex.[11]

In view of the singular reactivity shown by the [Ph$_2$P(O)NP(O)Ph$_2$]$^-$ anion toward [MnBr(CO)$_5$], we decided to explore its reactivity toward rhenium carbonyls. As a source for the latter, we chose the complexes [ReBr(CO)$_5$], [Re$_2$Br$_2$(CO)$_6$(THF)$_2$], and [ReOTf(CO)$_5$], for reasons that will be later established.

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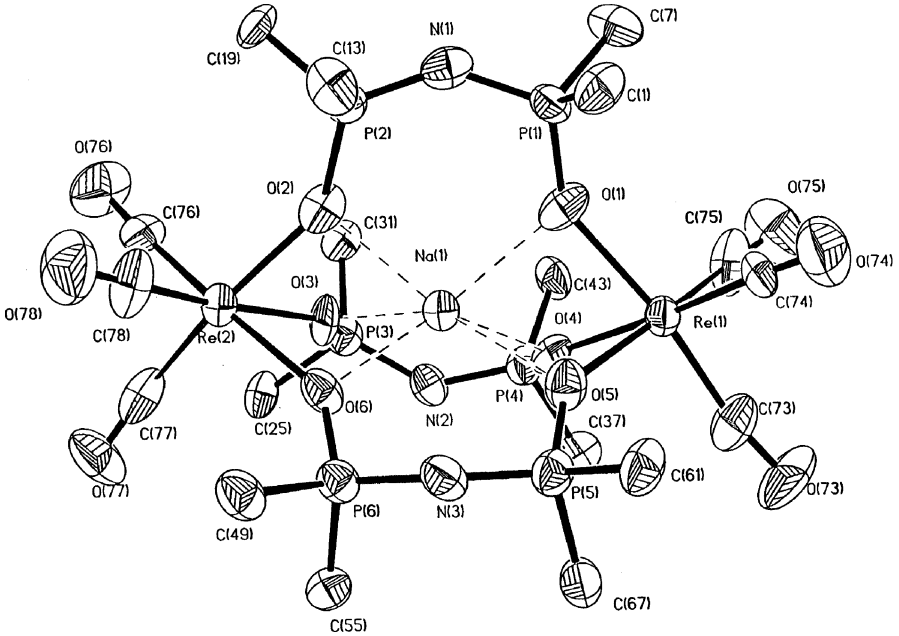

**Figure 1.** Molecular structure of **6**, including the atom numbering scheme (ORTEP drawing with 50% probability ellipsoids). Only phenyl ipso carbon atoms are shown for clarity. The partial occupancy of the crystallization solvent is not shown. Selected bond lengths (Å) and angles (deg): Re(1)−O(1), 2.176(9); Re(2)−O(2), 2.144(9); Re(1)−O(4), 2.176(9); Re(2)−O(3), 2.174(9); Re(1)−O(5), 2.185(11); Re(2)−O(6), 2.164(9). Na(1)−O(1), 2.342(12); Na(1)−O(4), 2.339(11); Na(1)−O(5), 2.352(11); Na(1)−O(2), 2.332(10); Na(1)−O(3), 2.315(10); Na(1)−O(6), 2.292(12); P(2)−N(1)−P(1), 133.2(8); P(3)−N(2)−P(4), 132.3(8); P(6)−N(3)−P(5), 133.3(8).

We wish to report in this communication on the spontaneous formation of an organometallic−inorganic dirhenium carbonyl cryptate encapsulating a sodium cation.

Reaction of equimolar amounts of $[ReBr(CO)_5]$ with $Na[Ph_2P(O)NP(O)Ph_2]$ in boiling toluene afforded $\{Re_2(CO)_6[\mu\text{-}Ph_2P(O)NP(O)Ph_2\text{-}\kappa^2O]_3\}Na$ (**6**) in 95% yield according to Scheme 1.

**Scheme 1**

$$2[ReBr(CO)_5] \;+\; 3\,Na[Ph_2(O)PNP(O)Ph_2] \xrightarrow{\text{boiling toluene}}$$

$$Na[Re_2(CO)_6\{\mu\text{-}Ph_2P(O)NP(O)Ph_2\text{-}\kappa^2O\}_3] \;+\; 4CO \;+ 2NaBr$$

The resulting compound is soluble in low-polarity halogen solvents and insoluble in nonpolar organic solvents and polar solvents; analytical and spectral data show that the product obtained is a dinuclear rhenate(I) carbonyl complex, highly stable both in solution and in the solid state for months.

The IR spectrum of **6** showed two strong bands in the $\nu$(CO) region at 2025 and 1901 $cm^{-1}$ in $CHCl_3$, assigned to the $A''_2 + E'$ vibration modes, corresponding to a *fac* disposition of the CO groups. The $^1H$ NMR spectrum displayed three resonances in the ratio 2:1:2 corresponding to the ortho (7.62 ppm), para (7.3 ppm), and meta aromatic hydrogens (7.1 ppm), respectively. The $^{13}C$ NMR spectrum contained two sets of signals: the CO groups (177.5 ppm) and the aromatic carbon atoms (127.7−133.6 ppm). The high average symmetry of **6** in solution is evidenced by $^{31}P$ NMR spectroscopy, as only one singlet appears at 24.2 ppm.

The crystal structure of **6** was determined and is shown in Figure 1, together with some selected bond distances and angles. The complex **6** is formed by two $-Re(CO)_3$ fragments united by three end-bound $[Ph_2P(O)NP(O)Ph_2]$ ligands; in the resulting cavity the Na cation is encaged, forming an organometallacryptate.[12]

The coordination geometry around both rhenium atoms is pseudo-octahedral, while the coordination geometry around the sodium cation can be best visualized as a trigonal antiprism. There are no metallophilic interactions between the rhenium and sodium atoms.[14] The PNP angles are all equal within experimental error (ca. 132°). The OPNPO backbone is renowned for its flexibility (in $HN(OPPh_2)_2$ the PNP angle spans 180°[13]), and the bridge coordination of the ligands in **6** does not singularly affect the magnitude of the PNP angle compared with the PNP angles of the coordinated $N(OPPh_2)_2$ ligand in a chelate fashion.[4] This kind of bonding has been found for the complex $K[Cd_2\{Ph_2P(O)NP(O)Ph_2\}_5]$, in which the K cation is encapsulated by three $[Ph_2P(O)NP(O)Ph_2]$ ligands with chair conformations in two of the $KO_2P_2N$ rings and a boat conformation in the third ring.[4] Most of the ligands employed in transition-metal metallocryptate complexes consist of arene units with N or O atoms in their framework (which bind the alkali-metal cation); ligand coordination to the transition metal is achieved through a soft atom, e.g. phosphorus. In complex **6** the oxygen atoms of the ligands bind both the transition and the alkali metals. Unlike their organic counterparts, multinuclear heterometallic cryptates are capable of binding metal ions either through metallophilic interactions between the metal capping groups and the guest ion or, as in the present case, through strong Lewis base interactions of the donor groups of the ligands.

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[12] Metallacryptates are three-dimensional metallacrowns. Metallacrowns were first described by Pecoraro: (a) Pecoraro, V. L. *Inorg. Chim. Acta* **1989**, *155*, 171. (b) Lah, M. S.; Pecoraro, V. L. *J. Am. Chem.* Soc. **1989**, *111*, 7258. For an extensive review see: (c) Pecoraro, V. L.; Stemmler, A. J.; Gibney, B. R.; Bodwin, J. J.; Wang, H.; Kampf, J. W.; Barwinski, A. In *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; Wiley: New York, 1997; Vol. 45, p 83. Cryptates are inclusion complexes in which the substrate is contained inside their molecular cavity. (d) Lehn, J.-M. *Acc. Chem. Res*. **1978**, *11*, 49. (e) Lehn, J.-M.;. Regnouf de Vains, J.-B. *Helv. Chim. Acta* **1992**, *75*, 1221.

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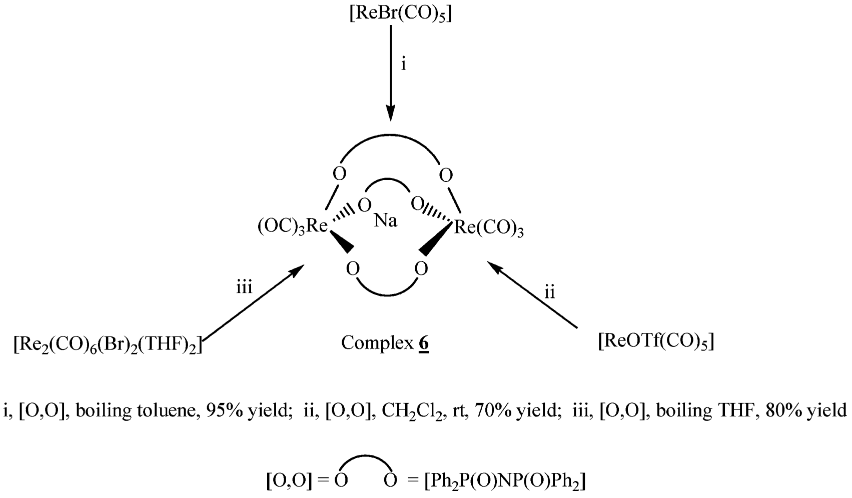
[14] For metallophilic interactions in multiheteronuclear matallocryptates see: Catalano, J. V.; Malwitz, M. A. *J. Am. Chem. Soc.* **2004**, *126*, 6560 and references therein.

**Scheme 2**



i, [O,O], boiling toluene, 95% yield; ii, [O,O], $CH_2Cl_2$, rt, 70% yield; iii, [O,O], boiling THF, 80% yield

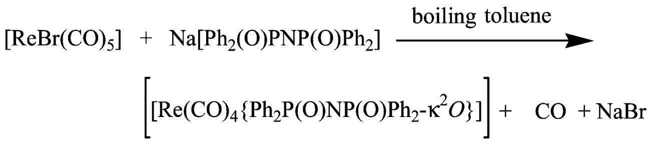
Multinuclear heterometallic cryptates, constructed of transition and alkali metals, have proven adequate in developing multifunctional catalytic systems and electro- and photochemical devices.[15]

Due to the dinuclear nature of complex **6**, we thought it convenient to test a dirhenium carbonyl complex as the starting material for the generation of the cryptate; thus, we reacted equimolar amounts of $[Re_2Br_2(CO)_6(THF)_2]$,[16] prepared in situ, and $Na[Ph_2P(O)NP(O)Ph_2]$ in boiling THF: $Na[Re_2(CO)_6\{\mu\text{-}Ph_2P(O)NP(O)Ph_2\text{-}O,O'\}_3]$ (**6**) was isolated in 80% yield. When $[ReOTf(CO)_5]$ was reacted with $Na[Ph_2P(O)NP(O)Ph_2]$ in $CH_2Cl_2$ at room temperature for 1 h, the cryptate **6** was generated in 70% yield (Scheme 2).

The fact that substitution of a good leaving group, $TfO^-$, for bromide resulted in a decrease in the reaction yield of the metallocryptate suggests that its formation involves, besides the nucleophilic attack on $[ReOTf(CO)_5]$, at least a reaction step where a nucleophilic substitution does not take place.

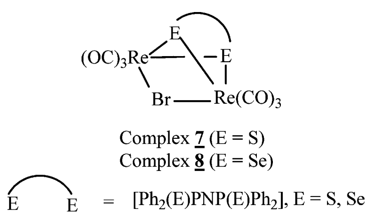
When $[ReBr(CO)_5]$ reacted with $Na[Ph_2P(O)NP(O)Ph_2]$ in refluxing toluene, NaBr starts forming after approximately 10 min. The formation of NaBr at an early stage in the reaction is indicative of a nucleophilic attack by the anion $[Ph_2P(O)NP(O)Ph_2]^-$, according to Scheme 3.

**Scheme 3**



The species $[Re(CO)_4\{Ph_2P(O)NP(O)Ph_2\text{-}\kappa^2O\}]$ formed and reacted at such a rate that its detection by IR spectroscopy was precluded. This behavior is consistent with the rates of formation of the complexes $[Re(CO)_4\{Ph_2P(Se)NP(Se)Ph_2\text{-}\kappa^2Se\}]$ and $[Re(CO)_4\{Ph_2P(S)NP(S)Ph_2\text{-}\kappa^2S\}]$, where the selenium complex formed in 30 min[9] while the sulfur complex was generated within the first 10 min of reaction,[17] both starting from $[ReBr(CO)_5]$ and the corresponding chalcogen ligand in boiling toluene. These results lead to the conclusion that the Na cation is incorporated at a middle or final stage in the formation path of **6**. Identification of the species **7** and **8** (Scheme 4) as products of the reaction of $[ReBr(CO)_5]$ and $[Re(CO)_4\{Ph_2P(O)NP(O)Ph_2\text{-}\kappa^2E\}]$ (E = S, Se) in boiling toluene[17] reinforces this assumption and points out the fact that the sodium cation is incorporated at a final stage in the self-assembly process of **6** and, therefore, does not exert a templating effect on the $[Ph_2P(O)NP(O)Ph_2]$ ligands.

**Scheme 4**



As in the case of the mononuclear species $[Re(CO)_4\{Ph_2P(O)NP(O)Ph_2\text{-}\kappa^2O\}]$, we have not been able to detect the oxygen analogue of complexes **7** and **8**; however, the existence of complexes **1**−**4** and of the oxygen complex $[Mn(CO)_4\{Ph_2P(O)NP(O)Ph_2\text{-}\kappa^2O\}]$ (detected by IR spectroscopy[10]) encourages us to propose the reaction path for the formation of **6** shown in Scheme 5.

When the reaction is carried out with $[ReOTf(CO)_5]$, complex **B** must be ruled out from the reaction path mentioned above; therefore, complex **6** would arise from species **C**, which in turn can be generated according to the reaction shown in Scheme 6.

The stability of complex **6** is reminiscent of that of the anionic species $[(CO)_3Re(\mu\text{-}OR)_3Re(CO)_3]^-$, which are quite stable and represent the final point of mild pyrolysis reactions[19] or cluster degradation[18] and can be prepared from $[ReBr(CO)_5]$ and NaOR:[19] the construction of the corresponding cryptates is not possible for these anions, due to the small size of the cavity formed by the three OR ligands.

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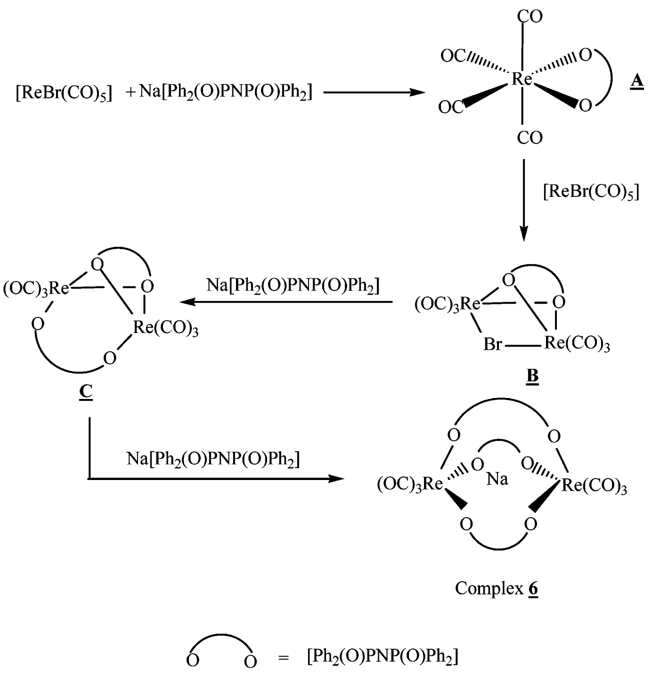
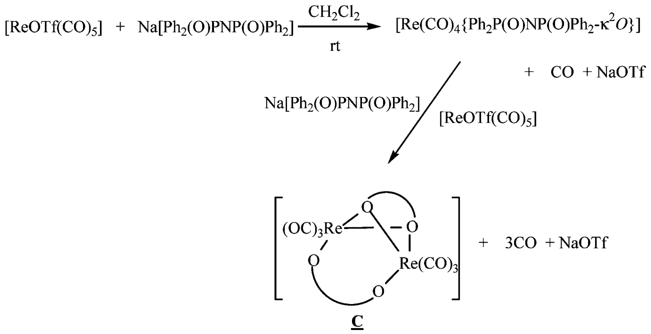
**Scheme 5**



**Scheme 6**



The binding of two $-\mathrm{Re(CO)_3}$ fragments by triple bridging is well documented in the literature;[20] however, the bridging units known so far are not long enough to enclose an atom in their cavities (although this has not prevented the anion $[\mathrm{(CO)_3Re(\mu\text{-}OMe)_3Re(CO)_3}]^-$ from displaying supramolecular behavior as a cryptand[20a]). It is foreseeable that encapsulation of a cation, be it mono- or polyatomic, between two $-\mathrm{Re(CO)_3}$ moieties can be effected by taking advantage of their tendency to join by bridges: the length and nature of the atoms constituting the backbones of the bridges have yet to be further explored. In an initial attempt to continue with this research and having in mind the facility of the $[\mathrm{(CO)_3Re(\mu\text{-}OR)_3Re(CO)_3}]^-$ anions for ligand exchange reactions,[20b,c] we are testing the reactivity of complex **6** toward the salts $\mathrm{M[Ph_2P(E)NP(E)Ph_2]}$ (M = Na, K; E = S, Se). It is noteworthy that the rhenium complexes with the anion $[\mathrm{Ph_2P(O)NP(O)Ph_2}]^-$ reported in the literature involve a Re(V) atom: $[\mathrm{ReOCl_2\{N(OPPh_2)_2\}(PPh_3)}]$,[21] $[\mathrm{Re(NMe)Cl_2\{N(OPPh_2)_2\}(PPh_3)}]$,[22] and $[\mathrm{ReN\{N(OPPh_2)_2\}_2(PPh_3)}]$;[23] coordination of the monoionic ligand $[\mathrm{Ph_2P(O)NP(O)Ph_2}]$ to the "hard" Re(V) core is accomplished through both oxygen atoms to the metal center in a chelate fashion; in the present case the formation of **6** by ligating of three imidodiphosphinate anions to two $-\mathrm{Re(CO)_3}$ fragments seems to adequately match the "hardness" of the ligand with the "softness" of the rhenium cores and speaks of the key role for the interaction of the host Na cation with the six oxygen atoms of the three $[\mathrm{Ph_2P(O)NP(O)Ph_2}]$ ligands.

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**Note Added after ASAP Publication.** In the version of this paper published on the Web March 17, 2006, two formulas appearing in the paragraph immediately after Scheme 3 were incorrect. The version that now appears has the correct formulas.

**Supporting Information Available:** Text giving synthetic procedures for the preparation of complex **6** and a summary of data collection, refinement data, and spectra ($^{13}$C, $^{31}$P, and $^{1}$H NMR, infrared, FAB$^+$ mass). This material is available free of charge via the Internet at http://pubs.acs.org.

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