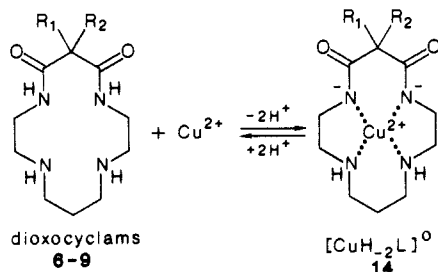


N lone pairs. A similar spacious effect argument may apply to explain the reduced  $pK_1$  and  $pK_2$  of the distal nitrogens in the fluorinated cyclams. The strong electron-withdrawing of F from the proximal nitrogens is reflected in the higher amide carbonyl stretching frequencies  $\nu_{C=O}$ , see Table I.<sup>14</sup> The fluorination to reduce amine basicities (or to increase  $NH^+$  acidities) may become very useful for macrocyclic polyamines that form anion complexes with polyoxyanions<sup>15</sup> (e.g., polycarboxylates,<sup>16</sup> phosphates,<sup>17</sup> catechols<sup>18</sup>).

Potentiometric titration of 7-9 in the presence of equimolar  $Cu^{2+}$  ion showed the complexation with concomitant dissociation of the two amide protons to  $[CuH_2L]^0$  (see 14) as in the case



of 6.<sup>19</sup> The complexation of 9 started to occur at lower pH  $\sim 3$  than that of 6 (pH  $> \sim 4$ ),<sup>2a</sup> with stability constant  $\log K_{CuH_2L}$  ( $= [CuH_2L][H^+]^2/[Cu][L]$ ) being  $2.5 \pm 0.2$  for 9 (at  $I = 0.1$  M ( $NaClO_4$ ) and  $25^\circ C$ ), as compared with 1.0 for 6 (at  $I = 0.1$  M ( $NaClO_4$ ) and  $25^\circ C$ ).<sup>2a</sup> The apparently greater complex stability with 9 over 6 was supported by the ligand displacement of  $CuH_2L$  ( $L = 6$ ) with  $L = 9$  (equimolar, at pH 5,  $50^\circ C$  over a few days), which was monitored by each distinct  $Cu^{III/II}$  potential (see the following). At present, we cannot rationalize why it is 9 with weaker bases and not 6 with stronger bases that affords a more stable  $CuH_2L$  complex.<sup>20</sup> The violet crystalline  $[CuH_2L]^0$  14 was isolated, which shows  $\nu_{C=O}$  at 1580, 1575, 1605, and  $1620\text{ cm}^{-1}$  with 6, 7, 8, and 9, respectively. Electron paramagnetic resonance spectra of those complexes at 77 K (in  $H_2O$ ) are similar with  $g_{\perp} = 2.06$ ,  $g_{\parallel} = 2.17$ ,  $A_{\parallel} = 215\text{ G}$  ( $G = 10^{-4}\text{ T}$ ) for 6 and  $g_{\perp} = 2.06$ ,  $g_{\parallel} = 2.18$ ,  $A_{\parallel} = 217\text{ G}$  for 7-9. Their d-d absorptions spectra [ $\lambda_{max}$  nm ( $\epsilon$ )] occur at 505 nm (100) with 6, 518 nm (140) with 7, 512 nm (70) with 8, and 515 nm (110) with 9, which seems to imply a little weakening of ligand fields by the fluorination.

Nickel (II)-cyclam (10-13) complexes were all isolated as  $[NiL](ClO_4)_2$ .<sup>21</sup> Their d-d absorptions in aqueous solution occur at 450 nm with 10, 453 nm with 11, 451 nm with 12, and 492 nm with 13, implying the dramatic LF reduction with the difluorination.  $Ni^{II}$  ions in these complexes remain mostly low-spin in aqueous solution with  $\mu_{eff}$  values ranging 2.3-2.5  $\mu_B$  with 10-13 (by Evans method<sup>22</sup> at  $35^\circ C$  and  $I = 0.1\text{ M}$ ).

The effect of the F substitution is most evident in electrochemical properties of Cu and Ni complexes (Table II). The fluorinated  $CuH_2L$  complexes 14 showed all quasi-reversible cyclic

**Table II.** Half-Wave Potentials (V versus SCE)<sup>a</sup> for  $Cu^{III/II}$  (Doubly Deprotonated 6-9) and  $Ni^{III/II}$  and  $Ni^{II/I}$  (10-13) Complexes

complex	$E_{1/2}$ (V versus SCE)		
	for $Cu^{III/II}$ <sup>b</sup>	for $Ni^{III/II}$ <sup>c</sup>	for $Ni^{II/I}$ <sup>d</sup>
$[CuH_2L]^0$ , L =			
6	+0.64		
7	+0.69		
8	+0.71		
9	+0.83		
$[NiL]^{2+}$ , L =			
10		+0.50	-1.56
11		+0.52	-1.52
12		+0.53	-1.53
13		+0.63	-1.46

<sup>a</sup> All solutions were deaerated by purified Ar, and a Pt wire was used as auxiliary electrode. <sup>b</sup> 0.5 M ( $Na_2SO_4$ ),  $25^\circ C$ , pH = 7.0. Working electrode (W.E.); glassy carbon. <sup>c</sup> 0.5 M ( $Na_2SO_4$ ),  $25^\circ C$ , pH = 6-7. W.E.; glassy carbon. <sup>d</sup> 0.1 M ( $NaClO_4$ ),  $25^\circ C$ , pH = 7.0. W.E.; Hanging mercury drop electrode.

voltammograms for  $Cu^{III/II}$ , as did nonfluorinated  $CuH_2L$ .<sup>23</sup> The fluorinated  $[NiL]^{2+}$  gave quasi-reversible voltammograms for  $Ni^{III/II}$  and  $Ni^{II/I}$ , as did the nonfluorinated 10 complex.<sup>24</sup> In either system, upon fluorination, the higher oxidation states  $Cu^{III}$  and  $Ni^{III}$  become successively destabilized with respect to  $Cu^{II}$  and  $Ni^{II}$ , while the lower oxidation state  $Ni^I$  becomes successively stabilized with respect to  $Ni^{II}$ .

Fluorinated macrocyclic ligands with easy access will find great potentials in basic as well as applied studies.

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## Oxygen Atom Transfer from an Iridium Dioxigen Complex: Oxidation of Carbon Monoxide to Carbonate

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There has been a great deal of interest in transition-metal dioxigen complexes either as mimics of biological systems<sup>1</sup> or for oxidation of organic substrates.<sup>2</sup> A number of questions remain to be answered concerning the factors that promote reactivity and/or selectivity in oxidations by transition-metal dioxigen complexes. An understanding of the intimate mechanism of oxygen atom transfer reactions and the electronic and steric effects on reactivity is required. In this communication we present our observations concerning the oxidation of carbon monoxide by  $(CH_3)_3Ir(P(p\text{-tolyl})_3)_2(CO)(O_2)$ . The data support a rapid reversible cleavage of one iridium-oxygen bond followed by attack on free CO.

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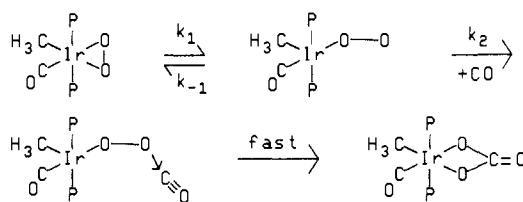
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**Table I.** Infrared Stretching Frequencies as the Result of Various Reactions with Isotopically Labeled Compounds<sup>a</sup>

iridium complex	CO gas	products					
		carbonyl			carbonate <sup>b</sup>		
		C≡O	C≡ <sup>18</sup> O	<sup>13</sup> C≡O	C=O	<sup>13</sup> C=O	C= <sup>18</sup> O
CH <sub>3</sub> Ir(P( <i>p</i> -tolyl) <sub>3</sub> ) <sub>2</sub> (CO)(O <sub>2</sub> )	CO	2000			1675 1620		
CH <sub>3</sub> Ir(P( <i>p</i> -tolyl) <sub>3</sub> ) <sub>2</sub> ( <sup>13</sup> CO)(O <sub>2</sub> )	CO			1950	1677 1623		
CH <sub>3</sub> Ir(P( <i>p</i> -tolyl) <sub>3</sub> ) <sub>2</sub> (C <sup>18</sup> O)(O <sub>2</sub> )	CO	2000	1950		1675 1620		
CH <sub>3</sub> Ir(P( <i>p</i> -tolyl) <sub>3</sub> ) <sub>2</sub> (CO)( <sup>18</sup> O <sub>2</sub> )	CO	1995					1654 1610
CH <sub>3</sub> Ir(P( <i>p</i> -tolyl) <sub>3</sub> ) <sub>2</sub> (CO)(O <sub>2</sub> )	<sup>13</sup> CO	2000				1637 1575	
CH <sub>3</sub> Ir(P( <i>p</i> -tolyl) <sub>3</sub> ) <sub>2</sub> (CO)(O <sub>2</sub> )	C <sup>18</sup> O	1995					1655 1617
CH <sub>3</sub> Ir(P( <i>p</i> -tolyl) <sub>3</sub> ) <sub>2</sub> (C <sup>18</sup> O <sub>3</sub> )(CO)		2003					1653 1615

<sup>a</sup>All frequencies are in cm<sup>-1</sup> as seen from KBr pellets. <sup>b</sup>The C–O single bond stretch of the carbonate appears to be part of an absorbance band at 1267 cm<sup>-1</sup>. When <sup>13</sup>C or <sup>18</sup>O is incorporated into the carbonate a shoulder appears at 1250 cm<sup>-1</sup>.

**Scheme I.** Proposed Reaction Mechanism for the Oxidation of CO by CH<sub>3</sub>Ir(P(*p*-tolyl)<sub>3</sub>)<sub>2</sub>(CO)(O<sub>2</sub>)<sup>a</sup>



<sup>a</sup>P = P(*p*-tolyl)<sub>3</sub>.

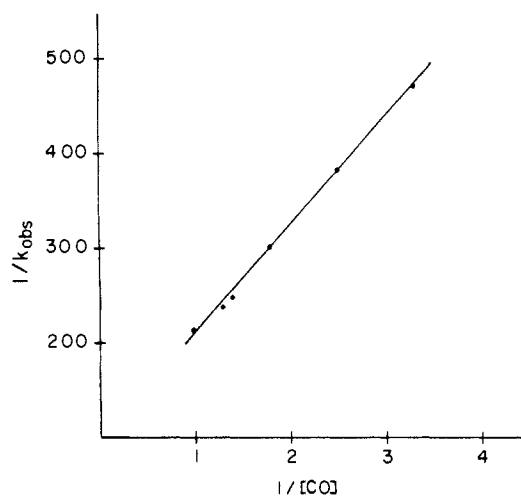
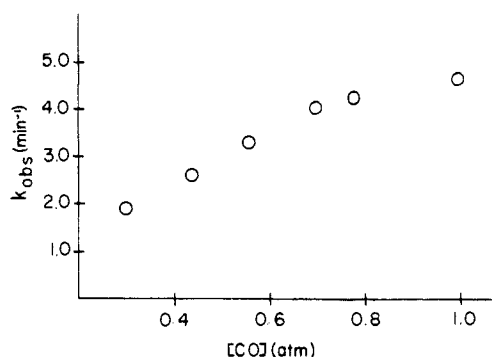
The (CH<sub>3</sub>)Ir(P(*p*-tolyl)<sub>3</sub>)<sub>2</sub>(CO)(O<sub>2</sub>) complex is synthesized by a procedure similar to that previously reported.<sup>3</sup> The reaction between (CH<sub>3</sub>)Ir(P(*p*-tolyl)<sub>3</sub>)<sub>2</sub>(CO)(O<sub>2</sub>) and CO results in the formation of a carbonato ligand that is bonded to the metal as a bidentate ligand. Similar complexes have been formed previously through reaction of a metal dioxygen complex with carbon monoxide<sup>4</sup> or by oxidation of a coordinated carbonyl by molecular oxygen.<sup>5</sup> The (CH<sub>3</sub>)Ir(P(*p*-tolyl)<sub>3</sub>)<sub>2</sub>(CO)(CO<sub>3</sub>) complex has been characterized spectroscopically.<sup>6</sup> The carbonate complex is prepared either by exposure of (CH<sub>3</sub>)Ir(P(*p*-tolyl)<sub>3</sub>)<sub>2</sub>(CO)(O<sub>2</sub>) to 1 atm or less of CO for 1 day to 2 weeks (see kinetic data) or by reaction with 3 atm of CO in toluene for 3 days at room temperature followed by slow crystallization of the product at 0 °C.

Isotopic labeling studies, shown in Table I, were performed by monitoring changes in absorption in the C–O double and triple bond region of the infrared spectrum upon <sup>13</sup>C or <sup>18</sup>O labeling. The C–O single bond stretch for the carbonate ligand could not be definitively identified due to the presence of other absorbances in that region.<sup>7</sup> The isotopic labeling shows that the carbonate is formed from the coordinated O<sub>2</sub> ligand and a free carbon monoxide molecule. An <sup>18</sup>O label in either the coordinated dioxygen or the free CO gives absorbances corresponding to <sup>18</sup>O in the C=O of the carbonate. Use of <sup>13</sup>CO gas gives <sup>13</sup>C labeling in the carbonate, confirming that free CO is involved in carbonate formation. Both <sup>13</sup>C and <sup>18</sup>O labeling studies show that the coordinated CO is not involved in the reaction and is not exchanged

**Table II.** Kinetic Data for Reaction of (CH<sub>3</sub>)Ir(P(*p*-tolyl)<sub>3</sub>)<sub>2</sub>(CO)(O<sub>2</sub>) with CO<sup>a</sup>

T (°C)	[CO] atm	solvent	k <sub>obsd</sub> (s <sup>-1</sup> )
50	1	1,2-dichloroethane	4.0 × 10 <sup>-4</sup>
50	1	tetrahydrofuran	1.8 × 10 <sup>-4</sup>
50	1	benzene	7.7 × 10 <sup>-5</sup>
42	1	benzene	4.2 × 10 <sup>-5</sup>
33	1	benzene	1.8 × 10 <sup>-5</sup>

<sup>a</sup>k<sub>obsd</sub> = k<sub>1</sub>k<sub>2</sub>[CO]/k<sub>-1</sub> + k<sub>2</sub>[CO], where k<sub>1</sub>, k<sub>-1</sub>, and k<sub>2</sub> are defined in Scheme I.



**Figure 1.** [CO] dependence on k<sub>obsd</sub> for the oxidation of CO by (CH<sub>3</sub>)Ir(P(*p*-tolyl)<sub>3</sub>)<sub>2</sub>(CO)(O<sub>2</sub>) in benzene at 50 °C. [CO] measured by partial pressure.

with free CO under the reaction conditions.

Kinetic studies were performed with 5.7 mM solutions of (CH<sub>3</sub>)Ir(P(*p*-tolyl)<sub>3</sub>)<sub>2</sub>(CO)(O<sub>2</sub>) in benzene under anaerobic

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(7) A portion of the absorption at 1267 cm<sup>-1</sup> may be assigned to the C–O single bond stretch based on appearance of a shoulder at 1250 when either <sup>13</sup>C or <sup>18</sup>O is incorporated.

conditions. All reactions were monitored by infrared spectroscopy following the growth of the absorbance at  $1675\text{ cm}^{-1}$  due to the C=O stretch of the carbonate ligand. The rate constants are listed in Table II. Activation parameters of  $\Delta S^\ddagger = -21\text{ eu}$  and  $\Delta H^\ddagger = 15\text{ kcal/mol}$  were calculated. The negative entropy of activation is indicative of an ordered transition state, and the increasing rate with increasing solvent polarity is suggestive of a polar transition state. The dependence on carbon monoxide concentration, as shown in Figure 1, is typical of a rate law that involves a pre-equilibrium prior to carbon monoxide oxidation. The rate constants

$$\text{rate} = \frac{k_1 k_2 [\text{CH}_3\text{Ir}(\text{P}(p\text{-tolyl})_3)_2(\text{CO})(\text{O}_2)] [\text{CO}]}{k_{-1} + k_2 [\text{CO}]}$$

are defined in Scheme I. A similar mechanism is seen for ligand substitution reactions in alkyl transition-metal complexes, where incoming ligand addition is preceded by a rapid pre-equilibrium that involves the formation of an acyl intermediate.<sup>8</sup>

The pre-equilibrium for the reaction between  $(\text{CH}_3)\text{Ir}(\text{P}(p\text{-tolyl})_3)_2(\text{CO})(\text{O}_2)$  and CO probably involves the rapid interconversion of the bonding of the dioxygen ligand from a bidentate to a monodentate form. The uncoordinated end of the dioxygen ligand could then attack free carbon monoxide. A peroxide attack on substrate has previously been implicated in oxidation reactions.<sup>9</sup> The proposed mechanism for this reaction is illustrated in Scheme I.

A similar pre-equilibrium involving a side to end-bonded dioxygen ligand has been previously suggested for other transition-metal dioxygen complexes, but this study provides the first tangible evidence for such a reaction. The pre-equilibrium step was considered but dismissed for the oxidation of hexafluoroacetone by reaction with a chloroiridium dioxygen complex.<sup>10</sup> Some of the observed reactivity of  $\text{MO}_2(t\text{-BuNC})_2$  complexes of nickel and palladium was attributed to this pre-equilibrium, but no data to substantiate the pathway were obtained.<sup>11</sup> Many proposed reaction pathways for oxygen atom transfer reactions of transition-metal complexes require coordination of the substrate prior to oxidation.<sup>12,13</sup> Our isotopic labeling studies demonstrate that the CO oxidized is not the CO initially coordinated to iridium and cast doubt on prior coordination as a requirement for oxidation by  $(\text{CH}_3)\text{Ir}(\text{P}(p\text{-tolyl})_3)_2(\text{CO})(\text{O}_2)$ .<sup>14</sup> Another possible route involves loss of the dioxygen ligand before the carbon monoxide becomes oxidized. This route can also be rejected since this would result in formation of a 16-electron complex which, from earlier studies,<sup>3</sup> shows instantaneous reactivity with methyl iodide and toward CO exchange. CO exchange is not observed, and no reaction has been observed for the dioxygen complex with  $\text{CH}_3\text{I}$ .

The mechanism shown in Scheme I provides the most reasonable explanation for the kinetic and isotopic labeling studies. The pre-equilibrium step is consistent with the observed rate law showing dependence on the [CO] only at low [CO]. A possible charge separation in the transition state could account for the increasing rate with solvent polarity. Presence of negative charge on the noncoordinated oxygen atom may facilitate attack on an external CO. Attack would be expected to occur at different rates for different substrates. This is observed with the order  $\text{SO}_2 > \text{PPh}_3 > \text{CO}_2 > \text{CO}$  for oxidation. After attack of the oxygen on CO, substantial rearrangement occurs leading to the stable bidentate carbonate. Studies are continuing to define the role of

steric and electronic factors on the reactivity of this dioxygen complex.

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### Preparation and Structure of $[(\text{C}_6\text{H}_5)_4\text{P}]_3[\text{NbTe}_{10}]\cdot\text{DMF}$ : A Soluble Tellurium Cluster Containing an Interstitial Transition-Metal Atom

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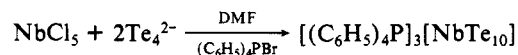
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Zintl ions are isolated polyanionic clusters of main-group elements. They have been known to exist in solution for many years, but only the relatively recent use of cryptands to sequester the alkali metal counterion has facilitated their isolation.<sup>1</sup> This has resulted in the structural characterization of a wide variety of novel compounds. However clusters containing transition metals are rare. An iron carbonyl cluster containing a tetrahedron of bismuth atoms has been reported<sup>2</sup> as well as a solid-state compound in which a niobium atom is surrounded by an eight-membered arsenic ring.<sup>3</sup> In addition, there are several gold and mercury telluride clusters obtained by extraction of mixed phases in basic solvents.<sup>4</sup> There is also NMR evidence for a platinum phosphine complex becoming incorporated into a  $\text{Sn}_9^{4-}$  cluster in solution.<sup>5</sup> However, bare clusters containing transition metals incorporated into main-group frameworks have not yet been isolated.

We have recently found that polytelluride and polyselenide anions prepared from the elements and an alkali metal in liquid ammonia are convenient reagents for the generation of a variety of metal polychalcogenides.<sup>6</sup> Recently our attention has focused on the reactions of polychalcogenides with high-valent transition-metal salts. Reaction of  $\text{Te}_n^{2-}$  or  $\text{Se}_n^{2-}$  ( $n = 2-4$ ) with  $\text{CrCl}_3$  in DMF produces  $\text{Cr}_7\text{Te}_{24}^{3-}$  and  $\text{Cr}_3\text{Se}_{24}^{3-}$ , respectively.<sup>7</sup> Reaction of  $\text{MoCl}_5$  or  $\text{WCl}_6$  with  $\text{Te}_x^{2-}$  in DMF generates  $[\text{MOTe}_8]^{2-}$  with the oxygen atom apparently derived from the solvent.<sup>8</sup> Previous to our work, Krebs prepared  $\text{Fe}_2\text{Se}_{12}^{2-}$ ,<sup>9</sup> and Ibers reported  $\text{V}_2\text{Se}_{13}^{2-}$ <sup>10</sup> as well as several tungsten polyselenide anions.<sup>11</sup> However, further work in this area has been scarce.<sup>12</sup> In this communication we report the preparation and structure of  $\text{NbTe}_{10}^{3-}$  which is the first Zintl ion containing an interstitial transition-metal atom.

The title compound was synthesized by the reaction of  $\text{NbCl}_5$  and 2 equiv of  $\text{K}_2\text{Te}_4$ , in DMF, followed by the addition of



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