as bands associated with CH_x groups were visible at 2961, 2948, 2925, and 2866 cm^{-1}. These bands agree with those reported for CH_3 at 2960 and 2875 cm^{-1}, for CH_2 at 2927 and 2862 cm^{-1}, and for CH at 2950 cm^{-1}.[105,106,166] Although the location of these hydrocarbon species on the catalyst surface could not be assigned with certainty, it is clear from the relative intensities, which show that CH_3 groups predominate, that the average chain length of these species was much shorter than those observed by King et al.[105] on SiO_2-supported Ru under reaction conditions. It is presumed that these IR-detectable species are most likely carbonaceous species adsorbed on the carbon, rather than the Ru, and are not reaction intermediates, consistent with the conclusions of Ekerdt and Bell.[102,167]

Summary

DRIFTS has been successfully applied to study carbon-supported Ru cluster catalysts. The decarbonylation of $Ru_3(CO)_{12}$ was followed quantitatively, and an activation energy near 20 kcal/mol was obtained in He. However, in H_2, the $H_4Ru_4(CO)_{12}$ cluster was rapidly formed, and its subsequent decomposition also followed first-order kinetics and gave activation energy values of 18–22 kcal/mol. To the best of our knowledge, this is the first time that the thermal decomposition of any ruthenium carbonyl cluster has been quantitatively studied, either in solution or on a support. The observed behavior can be explained by assuming the rate-determining step for the decomposition of the supported cluster is the same as that for nucleophilic substitution reactions of the cluster in solution, i.e., rupture of the first Ru–CO ligand, and the decarbonylation rates were very similar to rates of substitution in solution. The measured activation energies were lower than those in solution; however, the formation of highly dispersed metallic Ru particles would be expected to lower the activation energy of decarbonylation, as shown by thermodynamic calculations. Decomposition in He appeared to proceed via decarbonylation of $Ru_3(CO)_{12}$ followed by fragmentation, whereas the rapid formation of $H_4Ru_4(CO)_{12}$ and its subsequent decomposition was observed under H_2.

Complete decarbonylation in either gas produced zerovalent Ru, and adsorption of CO on these small Ru crystallites yielded spectra in good agreement with those reported in the literature for CO adsorbed on metallic Ru. Also, the calorimetric integral heat of adsorption of CO of 24.2 kcal/mol was very reasonable compared to reported values for CO adsorbed on Ru single crystals. The chemisorption measurements showed that the Ru particles were well-dispersed and resistant to sintering, even under reaction conditions. IR spectra under reaction conditions showed frequencies associated with CH, CH_2, and CH_3 species, and the preponderance of the last indicated the presence of only short-chain hydrocarbons on the catalyst surface, most likely on the carbon. The low turnover frequencies are similar to values measured over other well-dispersed and C-supported Ru catalysts.

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Coordination Compounds of Indium. 46. Indium(I) Derivatives of 3,5-Di-*tert*-butyl-1,2-*o*-benzoquinone

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Indium metal reacts with 3,5-di-*tert*-butyl-1,2-*o*-benzoquinone (TBQ) in refluxing toluene to give a solution of the corresponding semiquinone–indium(I) complex (TBSQ)In. This species can be stabilized in the solid state as a neutral complex with 1,10-phenanthroline (phen) or as a salt of the anion [(TBSQ)In(Cl)·phen]⁻. Oxidation in solution by I_2, $(C_6H_5)_2E_2$ (E = S, Se), and o-$O_2C_6Cl_4$ gives the indium(III) products $(TBSQ)InI_2$, $(TBSQ)In(EC_6H_5)_2$, and $(TBSQ)In(O_2C_6Cl_4)$, which again can be stabilized as the phen adducts. These compounds can also be prepared directly by refluxing mixtures of (e.g.) In + TBQ + I_2. All these semiquinone compounds give electron spin resonance spectra, and the hyperfine coupling constants A_{In} confirm the formulations. There are significant changes in A_{In} values as the result of the oxidation of indium(I) to indium(III).

Introduction

Recent work in this laboratory has been concerned with the oxidative-addition reaction between tin(II)[1] or indium(I)[2] halides and substituted *o*-benzoquinones to give the corresponding substituted catecholato derivatives. With the tetrahalogeno-*o*-quinones $Y_4C_6O_2$ (Y = Cl, Br), the reaction products are either $(Y_4C_6O_2)SnX_2$ or $(Y_4C_6O_2)InX$, which have been isolated as adducts with both neutral and anionic donor ligands. When the substrate is a less easily reduced *o*-quinone, such as 3,5-di-*tert*-butyl-*o*-benzoquinone, it is possible to observe the electron spin resonance (ESR) spectrum of the appropriate metal–semiquinone compounds, and with tin and indium both higher (+IV, +III) and lower (+II, +I) oxidation state species have been detected.[3] It therefore became important to investigate the preparation and properties of these lower oxidation species, and we now report the synthesis and study of (3,5-di-*tert*-butyl-*o*-semiquinonato)indium(I).

Relatively few indium(I) complexes are known,[4] but it is worth noting that the reactions of cyclopentadienylindium(I) with a number of β-diketonates has been shown to yield the indium(I) derivatives of the corresponding bidentate monoanion.[5] The present synthesis is considerably simpler, involving merely refluxing the metal and *o*-quinone together in a suitable solvent. We have recently shown[6] that both indium and tin react directly with $(C_6H_5)_2E_2$ (E = S, Se) to give $In(EC_6H_5)_3$ or $Sn(EC_6H_5)_4$, and it may well be that the metals represent a neglected starting point for the synthesis of main-group compounds.

Experimental Section

General Data. Indium metal (Alfa) was in the form of fine shavings. Solvents were dried by conventional methods and stored over appropriate drying agents; 3,5-di-*tert*-butyl-*o*-benzoquinone and other organic reagents were used without further purification. All experiments were carried out in an atmosphere of dry nitrogen. In the subsequent text, we use the abbreviation TBQ for the parent quinone, and TBSQ for the one-elec-

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(1) Annan, T. A.; Chadha, R. K.; Tuck, D. G.; Watson, K. *Can. J. Chem.* **1987**, *65*, 2670.

(2) Annan, T. A.; Tuck, D. G. *Can. J. Chem.* **1988**, *66*, 2935.

(3) Annan, T. A.; Chadha, R. K.; McConville, D. H.; McGarvey, B. R.; Ozarowski, A.; Tuck, D. G. *J. Chem. Soc., Dalton Trans.*, in press, and unpublished results.

(4) Tuck, D. G. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press, Oxford, U.K., 1987; Vol. 3, p 154 ff.

(5) Habeeb, J. J.; Tuck, D. G. *J. Chem. Soc., Dalton Trans.* **1975**, 1815.

(6) Mabrouk, H. E.; Kumar, R.; Tuck, D. G. *J. Chem. Soc., Dalton Trans.* **1988**, 1045.

Table I. Analytical Results for Indium–Semiquinonate Complexes

compd[a]	% In found	% In calcd	% C found	% C calcd	% H found	% H calcd	% N found	% N calcd
(TBSQ)In·phen	22.5	22.3	58.2	60.6	5.67	5.48	5.25	5.44
(TBSQ)In·phen·1.5Et$_2$O	18.7	18.3	60.9	61.4	6.21	6.92	4.48	4.47
(TBSQ)In·phen·TBQ	15.8	15.6	65.7	65.3	6.68	6.58	4.11	3.81
(C$_6$H$_5$)$_4$P[(TBSQ)In(Cl)phen][b]	12.7	12.9						
(TBSQ)InI$_2$·phen[c]	15.1	14.9						
(TBSQ)In(SC$_6$H$_5$)$_2$·phen	15.5	15.7						
(TBSQ)In(SC$_6$H$_5$)$_2$·2pic	15.5	15.5						
(TBSQ)In(SeC$_6$H$_5$)$_2$·phen	14.0	13.9						
(TBSQ)In(SeC$_6$H$_5$)$_2$·phen·0.5tol	13.1	13.1	57.4	57.1	5.10	4.85	4.15	3.21
(TBSQ)In(SeC$_6$H$_5$)$_2$·2pic·0.5tol	13.2	13.1	56.7	56.7	5.99	5.50	3.79	3.19
(TBSQ)In(O$_2$C$_6$Cl$_4$)·phen	15.2	15.1						

[a] TBQ = 3,5-di-*tert*-butyl-*o*-benzoquinone; TBSQ = 3,5-di-tert-butyl-*o*-benzosemiquinonate; phen = 1,10-phenanthroline; pic = 4-methylpyridine; tol = toluene. [b] Found: Cl, 3.70. Calcd: Cl, 4.00. [c] Found: I, 32.7. Calcd: I, 33.0.

tron-reduction product, 3,5-di-*tert*-butyl-*o*-benzosemiquinone.

Indium analysis was by atomic absorption spectrophotometry, using an IL-251 instrument, and microanalysis by Guelph Chemical Laboratories Ltd. Infrared spectra in the 200–4000-cm^{-1} region were recorded on the Nicolet 5DX spectrometer.

Electron spin resonance spectra were recorded on a Varian E12 instrument calibrated with an NMR gaussmeter. The klystron frequency was determined from the ESR spectrum of diphenylpicrylhydrazide. The sample and solution handling techniques were those described previously.[3]

Reaction of Indium Metal with TBQ. The reaction between the metal and *o*-quinone was first studied by stirring varying quantities of TBQ with indium under otherwise constant conditions, namely 0.18 g of indium (1.15 mmol), and 50 mL of toluene for 24 h at 100 °C. At the end of this period, the mixture was filtered hot, and the unreacted metal was collected, washed, dried, and weighed. The results of these experiments are shown in Figure 1 and discussed below. Related studies showed that the 24-h period used was indeed sufficient to achieve equilibrium and that the solubility of indium did not change when the refluxing was carried out for longer times.

In a subsequent experiment, equimolar quantities of indium metal and TBQ (1.6 mmol) were refluxed together in toluene, and the filtrate obtained after removal of the metal was taken to dryness. The residue was redissolved in diethyl ether (20 mL), to give a green solution; addition of 1,10-phenanthroline (phen; 0.29 g, 1.6 mmol) yielded a brown precipitate. The reaction mixture was stirred at room temperature for 2 h, after which the brown solid was collected by filtration, washed with diethyl ether, and dried in vacuo. The product is (3,5-di-*tert*-butyl-*o*-benzosemiquinonato)indium(I)–1,10-phenanthroline–1.5-(diethyl ether), (TBSQ)In·phen·1.5Et$_2$O (see Table I for analytical results). When this procedure was repeated with diethyl ether being replaced by petroleum ether as the medium for the reaction with phen, the product was the brown (TBSQ)In·phen. In both cases, the yield was essentially quantitative, based on the quantity of indium metal consumed in the initial refluxing process.

When the TBQ:In mole ratio in the initial equilibration procedure was 2:1, the final product was identified as (TBSQ)In·phen·TBQ, in which the unreacted TBQ acts as a bidentate donor (see below). In experiments in which the TBQ:In ratio exceeded 2:1, the filtrate obtained after collecting this product was taken to dryness, depositing red crystals, which were shown by melting point (110 °C; value for authentic sample 112 °C) and infrared spectroscopy to be unreacted TBQ.

[(C$_6$H$_5$)$_4$P][(TBSQ)In(Cl)·phen]. A suspension of (TBSQ)In·phen (0.18 g, 4.27 mmol) in acetonitrile (5 mL) was mixed with a solution of (C$_6$H$_5$)$_5$PCl (0.16 g, 4.27 mmol) in the same solvent (5 mL). The resultant solution was stirred at room temperature for approximately 2 h, after which diethyl ether (20 mL) was added to precipitate a light brown solid, which was collected by filtration and dried in vacuo. This product, [(C$_6$H$_5$)$_4$P][(TBSQ)In(Cl)·phen] is a 1:1 electrolyte to *N*,*N*-dimethylformamide (molar conductivity 74 Ω^{-1} cm^2 mol^{-1}; cf. standard range[7] for 1 mM solutions of 1:1 electrolytes in this solvent of 70–90 Ω^{-1} cm^2 mol^{-1}).

A sample of this salt was treated with CF$_3$COOD to give a solution whose ^{1}H NMR spectrum was recorded, showing multiplets at 9.59–8.02 ppm ((C$_6$H$_5$)$_4$P$^+$) and 6.8–6.6 ppm for the ring protons, together with singlets at 1.63 and 1.47 ppm from the *t*-butyl groups on C3 and C5, respectively (all values relative to TMS = 0 ppm).

Oxidation of (TBSQ)In by Iodine. Equimolar quantities (0.4 mmol) of iodine (as I$_2$) and the indium(I) semiquinonate complex, (TBSQ)In·phen, were stirred at room temperature in methylene chloride (20 mL). The color of iodine was discharged in 1 h, producing a yellow solution that was stirred for a further hour; addition of petroleum ether (50 mL) precipitated a yellow powder, (TBSQ)InI$_2$·phen, in quantitative yield. The ESR and infrared spectra of this material was identical with those of the same compound prepared by a different route (see below).

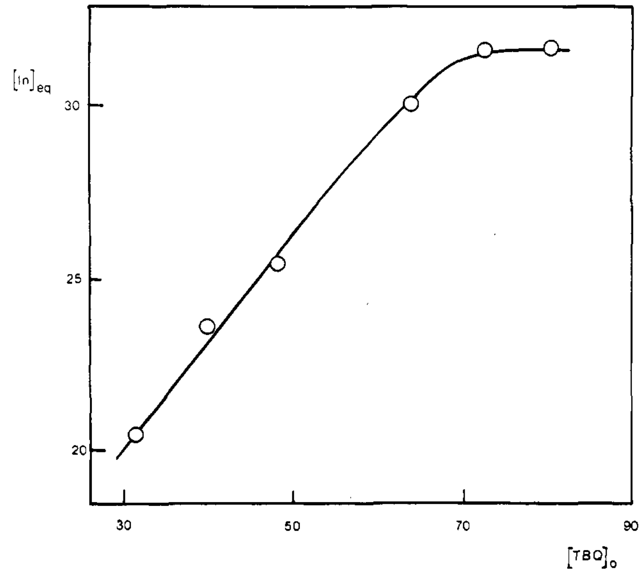

Figure 1. Equilibrium solubility of indium metal (mmol L^{-1}) in solutions of 3,5-di-*tert*-butyl-1,2-*o*-benzoquinone (TBQ) (mmol L^{-1}) in toluene, as a function of the initial TBQ concentration.

Direct Synthesis of (TBSQ)InI$_2$·phen. Finely cut indium metal (0.25 g, 2.2 mmol) was refluxed with TBQ (0.48 g, 2.2 mmol) and iodine (0.55 g, 2.2 mmol as I$_2$) in toluene (50 mL). After 2 h, by which time the metal was completely consumed and the color of indium discharged, an equimolar amount of 1,10-phenanthroline was added, whereupon a light brown solid was precipitated. Refluxing was discontinued at this stage, and the stirred mixture was cooled to ambient temperature; petroleum ether (20 mL) was then added and the stirring continued for 1 h. The solid product was collected by filtration, washed twice with 10 mL portions of petroleum ether, and dried in vacuo. The yield of (TBSQ)InI$_2$·phen was quantitative.

Reaction of (TBSQ)In with (C$_6$H$_5$)$_2$E$_2$ (E = S, Se). Finely divided indium metal (0.50 g, 4.35 mmol) was refluxed with TBQ (0.96 g, 4.36 mmol) in toluene (50 mL) for 24 h, after which unreacted indium (0.11 g, 0.96 mmol) was removed by filtration. A solution of (C$_6$H$_5$)$_2$E$_2$ (E = S, 0.74 g, 3.40 mmol; E = Se, 1.06 g, 3.40 mmol) in toluene (20 mL) was added dropwise to the filtrate, and the resultant pale green solution was refluxed (E = S, 16 h; E = Se, 2 h). Following addition of phen (0.61 g, 3.4 mmol), the mixture was stirred at room temperature for 2 h, after which the pale brown solid was collected by filtration, washed with petroleum ether, and dried in vacuo. The products were identified as the appropriate indium(III) derivatives, (TBSQ)In(EC$_6$H$_5$)$_2$·phen.

Direct Synthesis of (TBSQ)In(EC$_6$H$_5$)$_2$ Complexes. Diphenyl disulfide (0.48 g, 2.2 mmol) or diphenyl diselenide (0.69 g, 2.2 mmol), indium metal shavings (0.25 g, 2.2 mmol), and TBQ (0.48 g, 2.2 mmol) were refluxed together in toluene (50 mL) until the metal was completely consumed (E = S, 18 h; E = Se, 3 h). Addition of an equimolar quantity of phen, or 2 equiv of 4-methylpyridine, produced a pale brown precip-

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(7) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

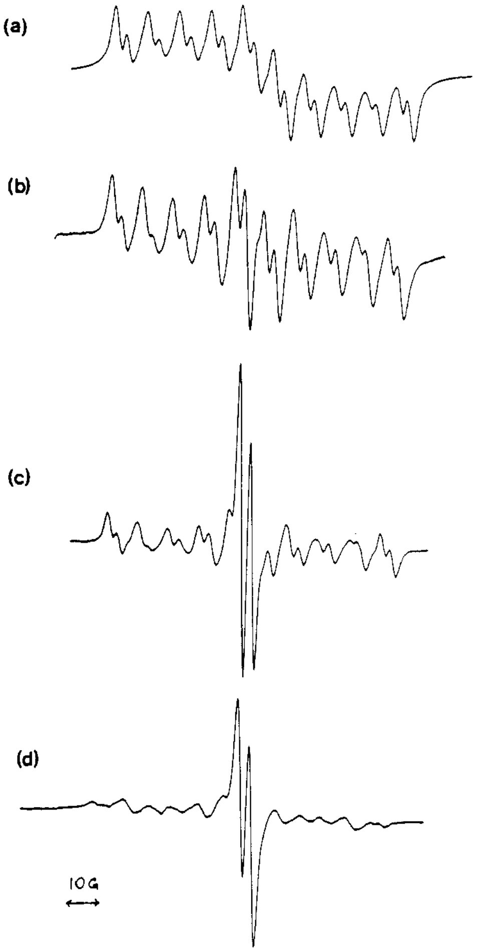

Figure 2. ESR spectra of mixtures of 4-methylpyridine (L) and (3,5-di-*tert*-butyl-1,2-*o*-semiquinonato)indium(I). Molar ratios of L:In: (a) 9:1, (b) 18:1, (c) 54.1, (d) 125:1.

itate, which was collected by filtration, washed with petroleum ether (2 × 10 mL), and dried in vacuo. The products are the appropriate adducts of (TBSQ)In(EC_6H_5)$_2$, which in these experiments were obtained as solvates with 0.5 mol of toluene in the case of E = Se.

Reaction of (TBSQ)In·phen with Tetrachloro-*o*-benzoquinone. (TBSQ)In·phen (0.5 g, 0.98 mmol) was suspended in toluene (20 mL), and a solution of *o*-$Cl_4C_6O_2$ (0.24 g, 0.98 mmol) in the same solvent (10 mL) was added dropwise over 20 min. The mixture was stirred for 2 h at room temperature, and the light green solid was collected, washed with petroleum ether (2 × 10 mL), and dried in vacuo. The yield of (TBSQ)In($O_2C_6Cl_4$)·phen was quantitative.

Electron Spin Resonance Spectroscopy. Solutions were made up under nitrogen in degassed solvents to give final concentrations on the order of 10^{-6} mol L^{-1}. The apparatus used[3] allowed solution reactions to be carried out immediately before running the resultant mixture into a tube that could be inserted directly into the cavity of the ESR spectrometer.

The results shown in Figure 2, and discussed below, refer to studies of the effect of 4-methylpyridine on the spectrum of (TBSQ)In^I. A solution of the latter was prepared by refluxing indium (0.60 g, 5.22 mmol) and TBQ (1.15 g, 5.22 mmol) in toluene (50 mL) for 24 h. From the weight of indium recovered (0.18 g), we calculate the concentration of (TBSQ)In^I as 0.073 mmol mL^{-1}. The ESR spectrum of this solution is a broad featureless resonance. Addition of 4-methylpyridine (0.025 mL, 0.26 mmol) produced the spectrum shown in Figure 2a. Successive addition of 4-methylpyridine (L) gave a mixture in which the ratio L:In was 9:1 (a), 18:1 (b), 53:1 (c), and 125:1 (d).

Results and Discussion

Reaction of Indium with TBQ. The results of experiments in which varying quantities of TBQ reacted with a constant quantity of indium metal are best understood in terms of Figure 1, in which the equilibrium concentration of indium in the final solution is shown as a function of the initial TBQ concentration. Under the conditions of the experiment, the maximum solubility of indium (i.e., expressed as all indium solute species) is 31.6 ± 0.3 mmol L^{-1} (3.63 mg mL^{-1} of In). More importantly, the slope of the curve at low concentrations corresponds to the molar ratio $[TBQ]_0$:$[In]_{eq}$ = 3.0 ± 0.1, and since the ESR evidence discussed below demonstrates the presence of a benzosemiquinone bonded to indium(I), we conclude that the solution species in dilute solution is (TBSQ)In^I·2TBQ, in which two TBQ molecules act as bidentate neutral donors. This is in agreement with the spectroscopic properties of related species isolated from such solutions. These results are similar to those reported earlier[8] for solutions of InBr in toluene/tmen solutions (tmen = *N,N,N′,N′*-tetramethylethanediamine), and solvation of the indium(I) species by the appropriate bidentate ligand is clearly critical in both cases.

When 1,10-phenanthroline was added to a solution of (TBSQ)In^I in the presence of excess TBQ, the product was (TBSQ)In^I·phen·TBQ, which is the analogue of the dilute solution species, with two bidentate donor ligands complexing the indium(I) semiquinonate. Addition of phen to solutions in which the $[In]_{eq}$:$[TBQ]_0$ ratio was less than 2 yielded the adduct (TBSQ)In^I·phen, which in the final solid product was solvated with diethyl ether when this solvent was used in the workup procedure. The same mother solution serves as the source of the anionic complex $[(TBSQ)In(Cl)\cdot phen]^-$, stabilized as the tetraphenylphosphonium salt. Although anionic derivatives of indium(I) are known,[4] this complex represents a new type of species, analogous to the catecholato derivatives of tin(II) discussed elsewhere.[9]

The first four compounds listed in Table I represent the unusual stabilization of indium(I) by the substituted semiquinonate anion and thus extend the short list of indium(I) complexes with anionic bidentate oxygen-donor ligands.[5]

Reactions of (TBSQ)In^I. The characterization of (TBSQ)In^I in solution depends in part on the ESR evidence (see below), in part on the isolation of the solid derivatives noted above, and in part on the reactions with mild oxidizing agents. With a molar equivalent of I_2, oxidation to indium(III) occurs, leaving the semiquinonate anion unaffected; the indium(III) product is readily stabilized against rearrangement in solution by the formation of the phen adduct:

$$(TBSQ)In^I \rightarrow (TBSQ)InI_2 \rightarrow (TBSQ)InI_2\cdot phen$$

The ESR spectra also confirm the oxidation of indium(I) to indium(III), since there are significant changes in the hyperfine constants (see below). This oxidation of the metal center by iodine has been shown to be a characteristic reaction of other indium(I) species studied in this laboratory. An equally useful diagnostic reaction is the oxidative addition with R_2E_2, which with InX (X = Cl, Br, I) in basic non-aqueous media gives rise to adducts of XIn$(ER)_2$ (E = S, Se).[10] In the present case, treatment of solutions of (TBSQ)In^I with equimolar quantities of $(C_6H_5)_2E_2$, calculated on the basis of the mass of indium dissolved in the initial reaction, gave essentially quantitative yields of (TBSQ)In^{III}(EC_6H_5)$_2$, isolated as the phen or γ-picoline adducts. The ESR and infrared spectra confirmed the formulation of these species.

The products of the above oxidative addition reactions were also synthesized directly by refluxing equimolar quantities of TBQ, In, and I_2 (or $(C_6H_5)_2E_2$) in toluene. The mechanism of these latter reactions has not been studied, but we note that indium reacts directly with $(C_6H_5)_2E_2$ to give In$(EC_6H_5)_3$ by a process that is thought to involve initial cleavage of the E–E bond to form $In^IEC_6H_5$, which then undergoes further oxidation to the indium(III) product,[6] and a similar sequence may also apply here. In any case, this direct synthesis confirms the presence of indium(III) in these products, and of the semiquinonate anion ligand, since materials prepared by this route were analytically and spectroscopically identical with those obtained via (TBSQ)In^I.

An oxidation reaction recently studied in this laboratory[2] is that

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(8) Peppe, C.; Tuck, D. G.; Victoriano, L. *J. Chem. Soc., Dalton Trans.* **1982**, 2165.
(9) Mabrouk, H. E.; Tuck, D. G. *J. Chem. Soc., Dalton Trans.* **1988**, 2539.
(10) Peppe, C.; Tuck, D. G. *Can. J. Chem.* **1984**, *62*, 2798.

Scheme I

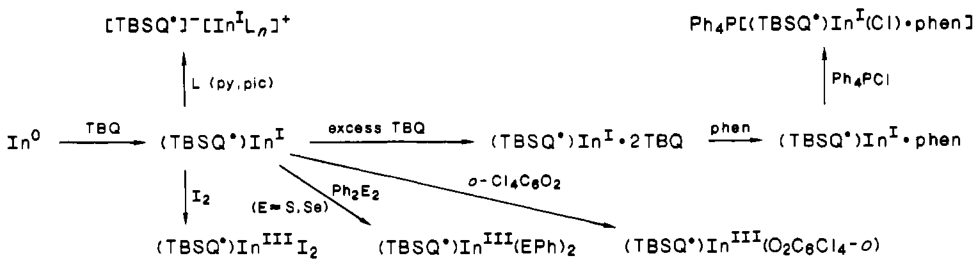


Table II. Hyperfine Constants (in G) for Indium–Semiquinonate Complexes

compd[a]	solvent	A_{In}	A_H(C4)
(TBSQ)In	toluene/pic	9.83	3.22
(TBSQ)In	toluene/pyridine	10.4	3.40
(TBSQ)InI_2	toluene/pic	6.44	3.20
(TBSQ)InI_2	THF/pic	5.10	3.50
(TBSQ)InI_2·phen	toluene	7.45	3.50
(TBSQ)In(SC_6H_5)·2pic	toluene	6.51	3.53
(TBSQ)In$(SeC_6H_5)_2$·2pic[b]	toluene	6.06	3.25

[a] Abbreviations as in Table I; THF = tetrahydrofuran. [b] A_{Se} = 1.5 G.

between indium(I) halides (InY) and tetrahalogeno-*o*-quinones, $X_4C_6O_2$ (X = Cl, Br). Such processes give derivatives of the halogenoindium(III) catecholate species $YInO_2C_6Cl_4$. The reaction of (TBSQ)In·phen with *o*-$Cl_4C_6O_2$ described above clearly follows the same stoichiometry as does that with InY and provides further confirmation of the oxidation state of the metal in (TBSQ)In·phen.

The reactions of (TBSQ)In, both complex formation and oxidation, are summarized in Scheme I.

Vibrational Spectroscopy. The most important diagnostic feature of the infrared spectra of each of the products listed in Table I is a series of bands in the region 1470 vs, 1448 vs, and 1418 vs cm^{-1}, plus a band at 1250 s, br cm^{-1} assigned to ν(C–O) of coordinated semiquinone by analogy with previous studies of similar complexes $Cr^{III}(O_2C_6Cl_4)_3$,[11] $[Co^{III}(TBSQ)trien]Cl_2$,[12] and $Cr^{III}(TBSQ)_3$.[13] Those compounds which contain phen or γ-picoline also show the typical infrared absorptions of those ligands in their coordinated form, and those with EC_6H_5 ligands have the features reported from earlier work on such molecules.[10] The substance formulated as (TBSQ)In·phen·TBQ has a strong absorption at 1624 cm^{-1}, which is assigned to ν(C=O) of the coordinated *o*-benzoquinone; this represents a shift of 50 cm^{-1} from the corresponding vibration in the free molecule, which is consistent with results for adducts of other *o*-quinones.[14]

The far-infrared spectra equally confirm the structures set out below. For all compounds, vibrations in the range 420–430 cm^{-1} correspond to ν(In–O), as observed in indium–catecholate complexes,[2] and ν(In–N) is seen at 280–290 cm^{-1} for the phen derivatives. A band at 330 cm^{-1} (s, br) in (TBSQ)In$(SC_6H_5)_2$·phen is assigned to ν(In–S), with the corresponding mode in the selenium analogue at 212 cm^{-1}, in both cases in agreement with the results of previous studies of the related $XIn(EC_6H_5)_2py_2$ systems (X = Br, I; E = S, Se).[10] Finally, the iodo derivative (TBSQ)InI_2·phen has absorptions in the far infrared at 182 + 130 cm^{-1}, identified as ν_{as} and ν_s of the InI_2 group of this molecule.

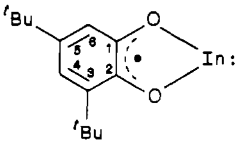
Electron Spin Resonance Spectroscopy. The ESR spectrum of a solution of (TBSQ)In in toluene is a broad featureless absorption, indicating the presence of a species containing a free radical. This solution contains a slight excess of unreacted TBQ, and we believe that this broad resonance is the result of the rapid exchange process

$$\text{(TBSQ)In} + \text{TBQ} \rightleftharpoons \text{(TBSQ)In·TBQ} \qquad (1)$$

and/or internal electron transfer between TBSQ and TBQ in the complex (TBSQ)In·TBQ. Successive addition of 4-methylpyridine (L) to give increasingly large L:In ratios produced the series of spectra shown in sequence in parts a–d of Figure 2. Spectrum 2a is that of two species, identified as $(TBSQ)In^I$ and the free $TBSQ^-$ anion, while 2d is essentially that of the free anion. The equilibrium being observed here is

$$\text{(TBSQ)In} + n\text{L} \rightleftharpoons \text{TBSQ}^- + [\text{InL}_n] \qquad (2)$$

which is moved to the right by increasing large L:In mole ratios. These spectra can be satisfactorily simulated by using the hyperfine constants A_{In} = 9.83 G, A_H = 3.22 for (TBSQ)In, and A_H = 3.50 G for $TBSQ^-$. The latter values are for the hydrogen atom at C4, and we did not identify any interaction at the C6 hydrogen.



Similar results for substituted *o*-benzoquinones have been reported by other workers.[15,16] Finally, we note that the solvation of indium(I) by a strong nitrogen donor parallels the behavior of the indium(I) halides in mixtures of toluene and *N*,*N*,*N′*,*N′*-tetramethylethanediamine.[8]

Spectra similar to those in Figure 2 were also observed in solutions containing excess pyridine and gave the hyperfine constants quoted in Table II. Different donors clearly affect the interaction of the unpaired electron of the TBSQ ligand with the metal by donating electron density onto the metal center. This effect is readily understood in terms of simple electrostatics, although of course more sophisticated arguments are needed to identify the details of this effect.

When a few drops of a solution of iodine in toluene was added to the toluene/4-methylpyridine solution of (TBSQ)In to produce (TBSQ)InI_2, the ESR spectrum (Figure 3) showed clearly the coupling of the unpaired electron to ^{115}In ($I = {}^9/_2$) and to the hydrogen at C4. This spectrum yielded a significantly different value for A_{In} of 5.10 G, a result which demonstrates the sensitivity of A_{In} to changes in electron density at the metal and which is confirmed by the values given in Table II for other indium(III) compounds prepared by the methods described above. The hyperfine constants clearly allow a distinction between the indium(I) species (A_{In} = 12.1–9.8 G) and those containing indium(III) (A_{In} = 7.5–5.10 G); there are clearly secondary effects that must be ascribed to changes in coordination number and/or solvent, but we cannot quantify these at present.

It is instructive to compare the present results with those of Muraev, Abakumov, and Razuvaev[18] on the reaction of thallium metal with various substituted *o*-quinones. The products with,

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(11) Cass, M. E.; Gordon, N. R.; Pierpont, C. G. *Inorg. Chem.* **1986**, *25*, 3962.

(12) Wicklund, P. A.; Beckmann, L. S.; Brown, D. G. *Inorg. Chem.* **1976**, *15*, 1996.

(13) Sofen, S. R.; Ware, D. C.; Cooper, S. R.; Raymond, K. N. *Inorg. Chem.* **1979**, *18*, 234.

(14) Crowley, P. J.; Haendler, H. M. *Inorg. Chem.* **1962**, *1*, 904.

(15) Ryba, O.; Pilar, J.; Petrǎmek, J. *Coll. Czech. Chem. Commun.* **1968**, *33*, 26.

(16) Lucken, E. A. C. *J. Chem. Soc.* **1964**, 4234.

(17) Muraev, V. A.; Abakumov, G. A.; Razuvaev, G. A. *Dokl. Akad. Nauk SSSR* **1974**, *218*, 1083.

(18) Klimov, E. S.; Abakumov, G. A.; Gladshev, E. N.; Bayushkin, P. Ya.; Muraev, V. A.; Razuvaev, G. A. *Dokl. Akad. Nauk SSSR* **1974**, *218*, 844.

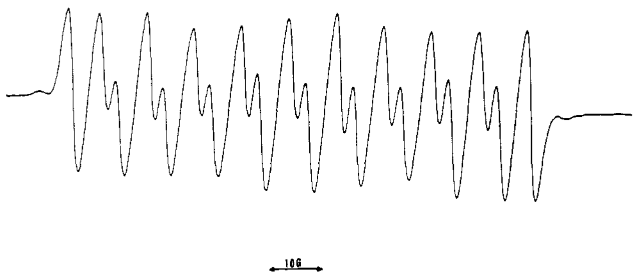

Figure 3. ESR spectrum of (TBSQ)InI$_2$ in tetrahydrofuran + 4-methylpyridine.

for example, TBQ are (TBSQ$^\bullet$)Tl and (TBCAT)Tl$_2$, which can be interconverted by appropriate redox reagents. The hyperfine coupling constants for (TBSQ$^\bullet$)Tl are A_{Tl} = 62.0 G and A_{H} = 3.2 G. It is also useful to compare this value for A_{Tl} with that in the thallium(III) species (TBSQ$^\bullet$)Tl(C$_2$H$_5$)$_2$, for which A_{Tl} = 23.9 G. The ratio between A_{Tl} for these two different oxidation states, in admittedly rather different compounds, is Tl$^{\mathrm{I}}$:Tl$^{\mathrm{III}}$ ~ 2.6, while that for the indium reported above is ca. 2.0, depending on the compounds involved. The values for thallium are much larger than those for indium, irrespective of the oxidation state, due to the Fermi contact terms involved.

The coupling of the electron with the semiquinone ring system is obviously less diagnostic insofar as the structures of the complexes are concerned. As noted above, only one coupling, that involving the hydrogen atom on C4, was observed, and no coupling to the *tert*-butyl groups was detected in any of the present systems. Detailed arguments based on similar results in *o*-benzoquinones have been presented by Felix and Sealy.[19] The observation of coupling of the electron with the selenium atoms of the $-$SeC$_6$H$_5$ derivative suggests a further use of ESR parameters in structural investigations of these indium compounds.

In general then, the ESR spectra confirm unambiguously that the reaction of indium with TBQ gives the indium(I)-semiquinonate complex, and that this species can be oxidized to give indium(III)-semiquinonate derivatives. These spectroscopic results are entirely congruent with the preparative work and with the vibrational spectra discussed above.

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(19) Felix, C. C.; Sealy, R. C. *J. Am. Chem. Soc.* **1982**, *104*, 1555.

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Epoxidation of Olefins Catalyzed by Chelating Diphosphine-Platinum(II) Complexes. Ring-Size and Ring-Shape Effects on the Catalytic Activity

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The epoxidation of 1-octene with H$_2$O$_2$ has been examined by using as catalysts a homologous class of 10 (diphosphine)Pt(CF$_3$)(solv)$^+$ and 10 (diphosphine)Pt(CF$_3$)(OH) type complexes, where the diphosphine has been systematically varied. All diphosphines contain two $-$PPh$_2$ groups but differ in the hydrocarbon chain linking together the two phosphorus atoms. The epoxidation reaction experimental conditions have been chosen in order to study the effect of the metal-diphosphine ring size and ring shape on the catalytic activity. It appears that diphosphine complexes with rigid, five-membered chelate rings prove to be the best catalysts.

Introduction

The interest in the direct oxidation of olefins to epoxides with transition-metal complexes has remained very high during the years, since these compounds are key industrial intermediates for the preparation of a wide variety of chemicals such as glycols, alkanolamines, and polymers like polyesters, polyurethanes and epoxy resins.[2]

We have recently described a platinum-based system that is capable of catalyzing very efficiently the selective epoxidation of simple terminal olefins using as primary oxidant diluted (5-35%) H$_2$O$_2$.[3,4] The catalysts, of the general type shown in Figure 1, play in the system a bifunctional role[5] since (i) they activate otherwise unreactive olefins toward nucleophilic attack and (ii) they increase H$_2$O$_2$ nucleophilicity by forming Pt-OOH species through acid-base reactions. This system is highly chemoselective since epoxides are the only detectable oxidation products. The catalysts, modified with chiral diphosphines, lead to asymmetric epoxidations with enantioselectivity up to 41% in the case of propylene.[6] The reaction rates observed in the latter work seem to suggest an important role of the metal-diphosphine ring size and shape in affecting the overall catalytic activity. we have therefore undertaken a systematic study in order to establish some structure/reactivity correlations and to optimize the catalyst, by synthesizing the homologous class of complexes shown in Figure 1 with a wide variety of diphosphines, which have been tested in the epoxidation of 1-octene.

Results

Some of the complexes shown in Figure 1 have been already described in the literature, i.e., the CF$_3$ derivatives of dppe,[7] diphoe,[7] prophos,[6] and chiraphos;[6] all of the others have been prepared according to the general synthetic route outlined in the following sequence of reactions:

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(1) (a) University of Venice. (b) University of Padua.

(2) Weissermel, K.; Arpe, H.-J. *Industrial Organic Chemistry: Important Raw Materials and Intermediates*; Verlag Chemie: Weinheim, FRG, 1978.

(3) Strukul, G.; Michelin, R. A. *J. Chem. Soc., Chem. Commun.* **1984**, 1538.

(4) Strukul, G.; Michelin, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 7563.

(5) Zanardo, A.; Pinna, F.; Michelin, R. A.; Strukul, G. *Inorg. Chem.* **1988**, *27*, 1966.

(6) Sinigalia, R.; Michelin, R. A.; Pinna, F.; Strukul, G. *Organometallics* **1987**, *6*, 728.

(7) Michelin, R. A.; Napoli, M.; Ros, R. *J. Organomet. Chem.* **1979**, *174*, 239.