Effect of Polymer Attachment on the Equilibrium Acidity of an Organotransition Metal Hydride and an Organic Carboxylic Acid. Synthesis and Properties of a Polymer-Supported Metal Anion

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Abstract: A polystyrene-attached η^5-cyclopentadienyl(tricarbonyl)hydridomolybdenum complex (**P-6**) has been prepared and its reactions with several THF-soluble bases have been investigated. Enolates of β-dicarbonyl compounds quantitatively deprotonate **P-6**, giving polymer-bound salts of the corresponding anion (Ⓟ-Cp(CO)$_3$Mo$^-$, **P-7**). Equilibration studies involving polymers **P-6** and **P-7** and their soluble monomeric analogues in THF demonstrated that little change in pK_a is induced by binding the molybdenum hydride to the polymer. Even though the polymer-supported partners in these experiments are not soluble and therefore render the reactions heterogeneous, the systems adhere reasonably well to conventional equilibrium behavior, as exhibited by a simple equilibrium analysis which yields effectively constant K_{eq} values. A polymer-bound carboxylic acid (**P-1**) and its conjugate base (**P-2**) also displayed essentially conventional equilibrium dynamics.

Introduction

Molecules have been attached to polymers for many purposes,[1] including organic[2] and stereospecific[3] synthesis, catalysis,[4] separation and purification,[5] and isolation of reactive species.[6] In addition, interest in functionalized polymers has been furthered by their analogy to multifunctional biological molecules, e.g., polypeptides and enzymes.[7] However, one cannot assume that the chemistry of a bound species will be identical with that of its homogeneous, monomeric counterpart. In regarding the polymer that surrounds the affixed reagent as a primary solvation sphere, one must take into account the properties of the polymer backbone which might influence the reaction to be studied. These include the polymer's compatibility with the solvent system, i.e., solvation of the polymer backbone (hydrophobicity, hydrophilicity), polymer morphology (secondary and tertiary structures "directing" effective dilution of bound species), and electronic stabilization or destabilization of the affixed functionality's incipient transition states or intermediates (i.e., whether the backbone "supports" ionic charge or delocalizes radicals).

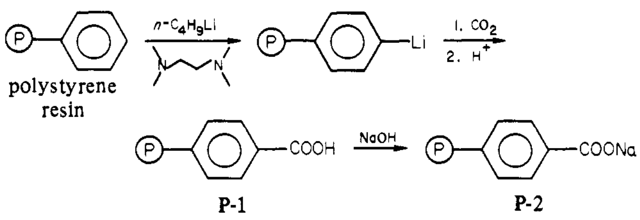
Previous treatment of the polymer's influence on the chemistry of affixed molecules has dealt primarily with kinetic effects. These include frequency of site-site interactions (intrapolymeric encounters),[6b,8] affixed reagents' mobility,[9] prolongation of supported reactive intermediate lifetimes,[6] and diffusion of soluble reagents within the polymer.[10] Few attempts have been made to characterize the role of these polymer-bound species in thermodynamic equilibria. To this end, we chose to study the acid-base equilibria of several polymer-bound acids.

Polyprotic molecules have long been of interest in biochemistry. In particular there has been much discussion over the determination of the pK_a of a particular acidic site as a function of surrounding acidic and basic sites in varying degrees of ionization. Traditionally, such methods as titration[11] and ultraviolet spectroscopy[12] have been used to observe ionization equilibria in polyprotic molecules; recently, such sophisticated techniques as ^{15}N NMR have probed buried active enzymatic sites for information leading to an acidic site's ionization state.[13] The approach which we employed involved spectrophotometric monitoring of soluble species in equilibrium with polymer-bound acids. An additional impetus to this study was the fact that, although many organotransition metal complexes have been attached to polymers, few such systems containing charged metal centers (especially anions) are available.

Synthesis of Starting Materials

Polymer-bound sodium benzoate (**P-2**) was synthesized as outlined in Scheme I.[14,15] Polymer supports were 3% cross-linked, macroporous, styrene–divinylbenzene copolymers. The degree of carboxylate functionalization was determined to be 2.3 mM of

Scheme I



P-1 **P-2**

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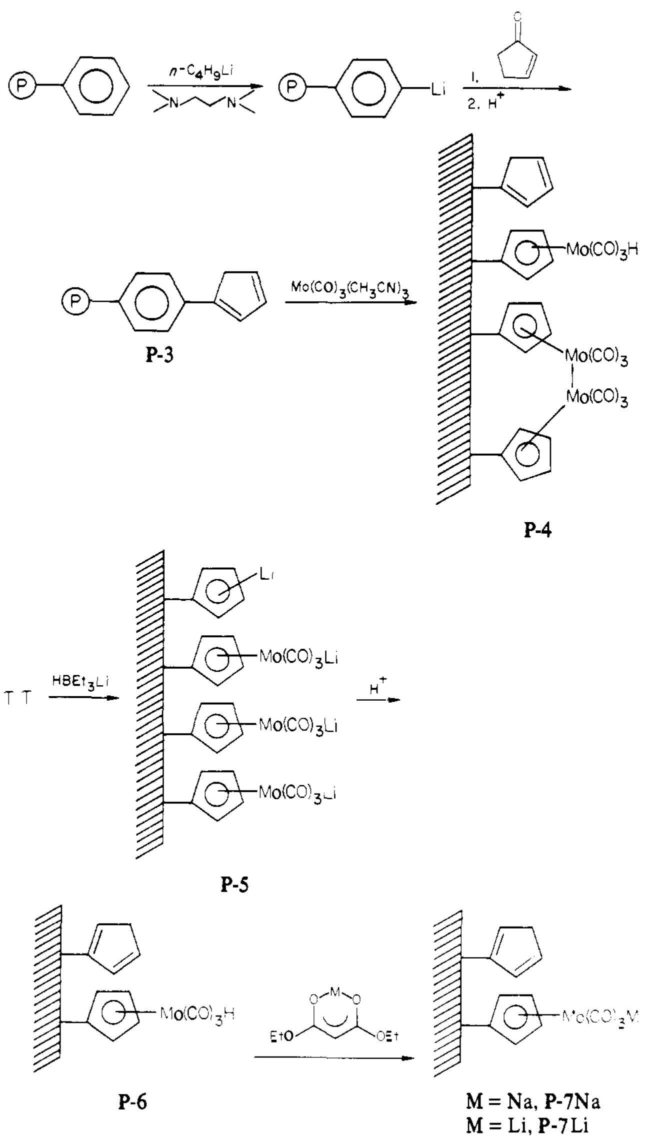
acid/g of polymer by titration of polybenzoic acid resin (**P-1**) in dioxane or THF with aqueous sodium hydroxide solutions. Final organic/aqueous ratios of approximately 2:1 in titration solutions were necessary to achieve reproducible results. Too high an aqueous component led to low figures for loading, presumably due to insufficient swelling of the polymer and therefore lack of exposure of all acidic sites.[16] Infrared carbonyl absorbances for resins **P-1** and **P-2** are given in Table I.

The polymer-bound $CpMo(CO)_3$ anion **P-7** was prepared according to Scheme II. Resinocyclopentadiene (**P-3**) was synthesized by direct lithiation of polystyrene (macroporous, 3% cross-linked with divinylbenzene) followed by reaction with cyclopentenone. This method afforded slightly lower loading than published methods[6b] which entailed a bromination step previous to lithiation, but our resulting polymer (**P-3**) was free of residual bromine.[17]

The conditions of the metalation of cyclopentadienyl polymer **P-3** resulted in some dimerization of metal centers on the polymer, as evidenced by both the characteristic red color and infrared absorbances of the molybdenum dimer moiety of resin **P-4** (Table I). This result contrasted with that of Gubitosa and Brintzinger,[18] who found that 18% cross-linked polystyrene prevented dimerization of metal centers, presumably owing to site–site isolation. Our results were compatible in view of the decreased rigidity of the polymer support on decreased cross-linking, resulting in an increase in the probability of interaction between active sites.

Lithium triethylborohydride converted both the molybdenum hydride and molybdenum dimer groups in resin **P-4** to the molybdenum anion of resin **P-5**.[19] In doing so, the borohydride reagent proved sufficiently basic to deprotonate residual, unfunctionalized resinocyclopentadiene.[20] Two further synthetic steps were required to generate resin **P-7**, polymer-bound molybdenum anion free of polymer-bound cyclopentadienyl anion (in order that the bound cyclopentadienyl anion not interfere in later equilibrium experiments). Protonation of all anionic sites on polymer **P-5** afforded polymer-bound molybdenum hydride (**P-6**). The supported metal hydride was then selectively deprotonated with an alkali metal salt of diethyl malonate, yielding resin **P-7** (under these conditions, the residual polymer-bound cyclopentadiene remained neutral[21]). The molybdenum anion's presence on resin **P-7**, indicated by IR spectroscopy, was confirmed by treatment of a sample of **P-7** with methyl iodide: an IR spectrum of the resulting polymer-bound complex **P-8** showed strong, sharp bands characteristic of an $RCpMo(CO)_3CH_3$ moiety (Table I).

Scheme II



P-3 **P-4** **P-5** **P-6**

M = Na, **P-7Na**
M = Li, **P-7Li**

Functionalized resins were analyzed by a combination of methods compatible with the resin's insolubility. Infrared absorbances of the bound metal carbonyls correlated well with those of their homogeneous models (Table I). IR spectra were recorded either on KBr pellets or on suspensions of the insoluble resin in reaction solvents. The latter method avoided the workup and drying steps in KBr pellet preparation and allowed in situ observation of the progress of reactions.[22]

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(9) (a) J. P. Collman, L. S. Hegedus, M. P. Cooke, J. R. Norton, G. Dolcetti, and D. N. Marquardt, *J. Am. Chem. Soc.*, **94**, 1790 (1972); (b) J. D. Aplin and L. D. Hall, *ibid.*, **99**, 4162 (1977); (c) S. L. Regen and D. P. Lee, *ibid.* **96**, 295 (1974); (d) S. L. Regen, *ibid.*, **99**, 3838 (1977); (e) H. Molinari and F. Montanari, *J. Chem. Soc., Chem. Commun.*, 639 (1977).

(10) (a) R. H. Grubbs and L. C. Kroll, *J. Am. Chem. Soc.*, **93**, 3062 (1971); (b) G. O. Evans, C. U. Pittman, R. McMillan, R. T. Beach, and R. Jones, *J. Organomet. Chem.*, 67, 295 (1974); (c) C. U. Pittman and R. Hanes, *Ann. N.Y. Acad. Sci.*, **239**, 76 (1974); (d) J. A. Greig and D. C. Sherrington, *Polymer*, **19**, 163 (1978).

(11) C. Tanford and J. D. Hauenstein, *J. Am. Chem. Soc.*, **78**, 5278 (1956).

(12) E. Katchalski and M. Sela, *J. Am. Chem. Soc.*, **75**, 5284 (1953).

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(14) (a) M. J. Farrall and J. M. J. Frechet, *J. Org. Chem.*, **41**, 3877 (1976); (b) T. M. Fyles and C. C. Leznoff, *Can. J. Chem.*, **54**, 935 (1976).

(15) The cross-hatched symbolism for the support is used to conveniently represent the polymer backbone and is not meant to indicate monolayer functionalization. The figures are drawn with para substitution for clarity only. Previous investigations have indicated that lithium substitution in resinophenyllithium is meta and para: C. D. Broaddus, *J. Org. Chem.*, **35**, 10 (1970); D. C. Evans, L. Phillips, J. A. Barrie, and M. H. George, *J. Polym. Sci., Polym. Lett. Ed.*, **12**, 199 (1974).

(16) For other examples of the effects of incomplete polymer swelling see, for example, D. C. Neckers, D. A. Kooistra, and G. W. Green, *J. Am. Chem. Soc.*, **94**, 3984 (1972); R. H. Grubbs, L. C. Kroll, and E. M. Sweet, *J. Macromol. Sci., Chem.*, 7, 1047 (1973); J. M. J. Frechet and K. E. Hague, *Macromolecules*, **8**, 130 (1975); M. D. Sanner, R. G. Austin, M. S. Wrighton, W. D. Honnick, and C. U. Pittman, Jr., *Inorg. Chem.* **18**, 928 (1979).

(17) In our hands, resinocyclopentadiene made via the bromination–lithiation route yielded a resin of which ~55% of the styrene monomers were substituted with cyclopentadiene, whereas the direct lithiation route (Scheme II) resulted in ~38% substitution of styrene monomers with cyclopentadiene.

(18) G. Gubitosa and H. Brintzinger, *J. Organomet. Chem.*, **140**, 187 (1977).

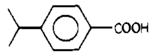
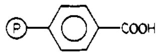
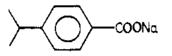
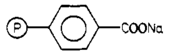
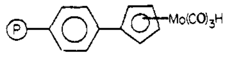
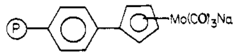
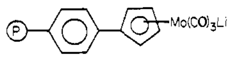
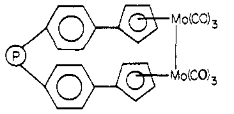
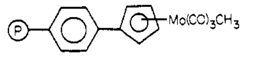
(19) For homogeneous precedent to this reaction, see J. A. Gladysz, G. M. Williams, W. Tam, and D. L. Johnson, *J. Organomet. Chem.*, **140**, C1 (1977).

(20) This was established by treating resinocyclopentadiene P-3 with $HBEt_3Li$. After extensive rinses with clean solvent to ensure complete removal of the borohydride, the resulting resin was exposed to a THF solution of diethyl malonate. Appearance of lithium diethyl malonate carbonyl absorbances in the IR spectrum of the solution above the polymer indicated to us that lithium cyclopentadienide had been formed on the polymer by reaction of $HBEt_3Li$ with resinocyclopentadienide. As a standard, the above procedure was repeated on unfunctionalized polystyrene. Those results indicated that no deprotonation of the polymer backbone was occurring.

(21) No carbonyl absorbances for diethyl malonate were observed in the IR spectrum of a THF solution of sodium diethyl malonate which had been in contact with resinocyclopentadiene P-3.

(22) This method posed some difficulties in that commercial IR cells had to be specially adapted to handle the slurried samples, and substraction of solvent adsorptions required a variable path length reference cell.

Table I. Infrared Carbonyl Absorbances

soluble compd, cm^{-1}		polymer-bound analogue, cm^{-1}	
 1	1722 (s), 1610 (w) (THF)	 **P-1**	1722 (s), 1685 (s) (KBr)
 2	1587 (s), 1545 (s), 1400 (s) (KBr)	 **P-2**	1600 (s), 1555 (s, br), 1395 (s) (KBr)
$CpMo(CO)_3H$ 6	2015 (m), 1932 (s), (THF)	 **P-6**	2010 (s), 1930 (s, br) (KBr)
$CpMo(CO)_3Na$ 7-Na	1903 (s), 1798 (s), 1745 (s) (THF)	 **P-7-Na**	1900 (s), 1840 (s), 1730 (w) (KBr)
$CpMo(CO)_3Li$ 7-Li	1910 (s), 1810 (s), 1785 (m), 1718 (s) (THF)	 **P-7-Li**	1905 (s), 1803 (sh), 1775 (s), 1710 (s, br) (KBr)
$[CpMo(CO)_3]_2$ 4	1958 (s), 1910 (s) (THF)	 **P-4**	1954 (s, br), 1904 (s, br) (KBr)
$CpMo(CO)_3CH_3$ 8	2014 (m), 1924 (s) (THF)	 **P-8**	2012 (s), 1935 (s, br) (KBr)

Elemental analysis served as a more qualitative than quantitative measure of loading owing to unacceptable irreproducibility in duplicate analyses, a problem shared by many researchers in this field.[5c,23] Cyclopentadiene loading on resin **P-3** was estimated by lithium analysis of a sample of resin **P-3** which had been previously treated with methyllithium.[6b] In the case of resin **P-7**, alkali-metal analysis as well as molybdenum analysis was used in estimating the degree of polymer functionalization (cf. Experimental Section). Typically, 0.6 mmol of molybdenum was incorporated in 1 g of polymer; this corresponds to substitution of approximately one-eighth of the styrene monomers of the polymer backbone.

Titration of functionalized polymers provided information about the number of active sites on a polymer within a certain pK_a range. Resin **P-3** was assayed for cyclopentadiene loading by titration with a solution of sodium triphenylmethide, the red color of the titrant serving as the end-point indicator. The titration of bound molybdenum hydride **P-6** with sodium diethyl malonate was monitored by IR for the appearance of the carbonyl absorbances of the corresponding conjugate acid. All polymer titrations had to be carried out very slowly over long periods of time (typically 12 h) to assure complete diffusion of soluble reactants into the polymer's interstices.

Finally, careful weighing of the polymer before and after each synthetic step provided information on the degree of functionalization that had been achieved in each step. These data were in good agreement with results from the previously mentioned methods of analysis.

Equilibration Experiments

Reactions of polymer-bound acids with soluble bases, and those of polymer-bound bases with soluble acids, were carried out in THF solutions of varying concentrations of the soluble component. Typically, 100 mg of resin was equilibrated with 5 or 10 mL of a 0.05–0.15 M solution of the soluble reagent. For example, resin **P-6**, containing a known loading of molybdenum hydride, was combined with a specified molarity of $CpMo(CO)_3^-Na^+$ in a 5-mL volumetric flask. This mixture was then allowed to stir for 6 h to assure complete equilibration of soluble components with all polymeric sites; longer reaction times led to decomposition of the species in solution. Infrared carbonyl absorbances were used to measure the ratio of concentrations of dissolved species (in the above example) of soluble molybdenum hydride formed to remaining soluble molybdenum anion. Extinction coefficients for the carbonyl bands of each soluble molybdenum compound in THF were predetermined from Beer's law plots (cf. Experimental Section). In the same manner, polymer-bound molybdenum anion (**P-7**) was equilibrated with homogeneous molybdenum hydride: the appearance in solution of molybdenum anion was coupled with an equal decrease in soluble molybdenum hydride concentration.

Equilibrium experiments were similarly carried out with polymeric benzoic acid (**P-1**) and with monomeric *p*-isopropylbenzoic acid. These reactions, however, produced quantitatively unreliable data owing to the unsupported benzoate salt's limited solubility in organic solvents. Neither substitution of Na^+ by the more hydrophobic tetraalkylammonium cation nor addition of crown ether improved its solubility. Studies on the acidity of the polymeric benzoic acid (**P-1**) were successfully carried out with $CpMo(CO)_3^-Na^+$ (**7-Na**) as a soluble base. Reactions between polycarboxylic resin (**P-1**) and THF solutions of molybdenum anion were performed both as a function of added soluble molybdenum anion and additionally as a function of the amount of added polymer in equilibrating solutions.

This same method for monitoring equilibria was applied to reactions between the supported molybdenum compounds and a series of infrared-active organic carbon acids and their conjugate bases, in reactions designed to monitor the proton-transfer activity of the functionalized polymer (vide infra).

Equilibrium Studies

1. Equilibration of Polycarboxylate Polymers Ⓟ-COOH (P-1) and Ⓟ-COONa (P-2). Polystyrenecarboxylic acid (**P-1**) and soluble molybdenum salt **7** were equilibrated in THF (as indicated in the previous section, solubility problems prevented us from quantitatively examining the equilibration of **P-1** with *p*-isopropylbenzoate (**2**)). The equilibrium was also approached from the reverse direction, i.e., from equilibration of sodium polystyrenecarboxylate (**P-2**) and soluble molybdenum hydride **6**. To emphasize that these experiments involve a polyfunctional acid and a soluble base (or, as in the latter case, a polyfunctional base and a soluble acid), we write the equilibrium as shown in eq 1. Table II summarizes the exact quantities of starting materials used in each case and the quantities of soluble molybdenum hydride and anion observed by IR after the system has reached equilibrium.

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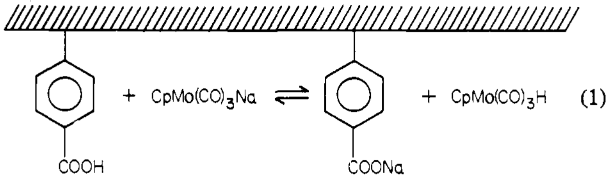
[23] R. J. Card and D. C. Neckers, *J. Am. Chem. Soc.*, **99**, 7734 (1977).

Table II. Equilibration of Ⓟ–COOH with $CpMo(CO)_3Na$ and Ⓟ–COONa with $CpMo(CO)_3H$

starting materials[a]						soluble components at equilibrium	
expt	resin	amt of resin, mg	mequiv[b] of CO_2H or CO_2^- on resin	CpMo-$(CO)_3^-Na^+$, mmol	CpMo-$(CO)_3H$, mmol	CpMo-$(CO)_3^-Na^+$, mmol	CpMo-$(CO)_3H$, mmol
1	P-1	32	0.074	0.080		0.047	0.033
2[c]	P-1	46	0.106	0.080		0.036	0.040
3[c]	P-1	61	0.141	0.080		0.031	0.048
4	P-1	30	0.070	0.076		0.045	0.031
5[d]	P-1	30	0.070	0.115		0.081	0.034
6	P-1	54	0.125	0.121		0.072	0.049
7[d]	P-1	54	0.125	0.262		0.199	0.063
8	P-1		0.134	0.164		0.092	0.072
9	P-2	35	0.076		0.076	0.037	0.039
10	P-2	37	0.081		0.074	0.038	0.036

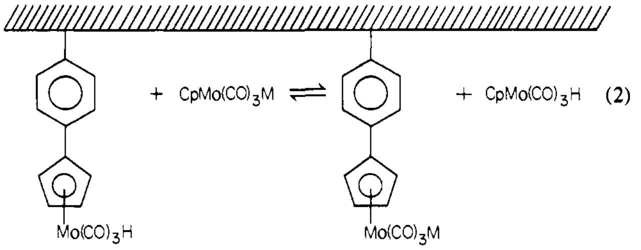
[a] In each case, 10 mL of THF was used as solvent. [b] Determined by titration of polymer (in acidic form) by OH^- (see Experimental Section). [c] Performed by adding sequential amounts of Ⓟ–CO_2H to the equilibrated solution of the previous experiment. [d] Performed by adding sequential amounts of $CpMo(CO)_3^-Na^+$ to the equilibrated solution of the previous experiment.



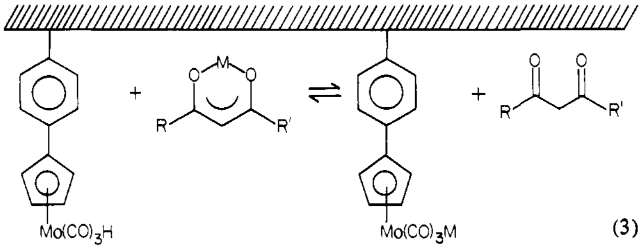
(1)

The polymer-bound acid Ⓟ-CO_2H and soluble hydride $CpMo(CO)_3H$ appear to have similar acidities. This may be seen, for example, in the first three experiments of Table II in which increasing amounts of polymeric acid were added to a constant amount of molybdenum anion. With roughly equal amounts of starting acid and base, the soluble anion is less than half protonated. Addition of more acid does not produce a concomitant amount of soluble hydride; doubling the amount of acid in solution produces significantly less than double the initial amount of hydride observed after the first addition. Similarly, adding sequential amounts of soluble anion to a stationary amount of polymeric acid produces soluble hydride, but not in quantities equal to the amount of anion added (experiments 4–10). This is just the sort of observation expected in a weak acid–weak base titration.

2. Equilibrations of Metalated Polymers Ⓟ-$CpMo(CO)_3H$ (P-6) and Ⓟ-$CpMo(CO)_3^-M^+$ (P-7). Similar experiments were carried out on the polymer-bound molybdenum hydride (and anion) with soluble molybdenum anion (and its conjugate acid), eq 2. Again, to rule out kinetic effects, each equilibrium was approached from both sides. As can be seen from Tables III and IV polymeric acid Ⓟ-$CpMo(CO)_3H$(**P-6**) and its soluble analogue **6** have similar acidities: this is shown by the less than quantitative proton transfer between the soluble species of eq 2 (a display of weak acid–weak base behavior as was observed in the case of Ⓟ-COOH and Ⓟ-COONa). The nearly identical behavior of the sodium and lithium salts indicates that this behavior is due to properties inherent in the neutral acids and anions, rather than being controlled by ion-pairing energetics. In support of this conclusion, addition of crown ether to preequilibrated solutions of polymers and soluble reagents produced no dramatic change in the concentrations of the reactants. In order to establish that the polymeric acid Ⓟ-$CpMo(CO)_3H$ (**P-6**) could be deprotonated quantitatively with anions whose base strengths were somewhat stronger than that of $CpMo(CO)_3^-$ (**7**) we also subjected **P-6** to treatment with enolate anions of diethyl malonate, ethyl acetoacetate, 2-carboethoxycyclopentanone, and 2-carboethoxycyclohexanone, eq 3. These were selected not only because they had pK_as in the appropriate range, but also because the concentrations of each β-dicarbonyl and its conjugate base could be clearly monitored by observing the carbonyl region of the infrared spectrum. In each of these cases, the equilibrium lay completely on the side of protonated enolate and deprotonated polymeric hydride.



(2)



(3)

Discussion

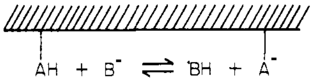
The first question we can now address on the basis of our results is: does the pK_a (acidity) of $CpMo(CO)_3H$ change appreciably upon binding to a swellable polymer? Although there are some important uncertainties in the quantitative analysis of our results, the *qualitative* result is clear: the fact that partial proton transfer is achieved on exposure of $CpMo(CO)_3H$ (**6**) to the polymer-bound analogue of its conjugate base Ⓟ-$CpMo(CO)_3^-$ (**P-7**) requires that their effective acidities be very similar.[24]

One difficulty with quantifying this result, that polymer-attached and soluble acids of similar structure have similar acidities, arises from the problem of measuring (and even defining) acidities in relatively nonpolar solvents such as THF. Ideally, we would like to have carried out our studies in aqueous or other highly polar media (e.g., Me_2SO or methanol) in which good pK_a data are available for a range of soluble acids.[25] The use of these solvents was precluded by the fact that our molybdenum hydride is insoluble in water and unstable in highly polar solvents such as Me_2SO, acetonitrile, and HMPA. We chose THF as the best alternative because it swells the polymer and dissolves our molybdenum compounds reasonably well.[26]

We now wish to concern ourselves with a second, and somewhat more complicated, question arising from our results: are equilibria between swellable polymers and dissolved species analyzable in a simple manner; i.e., is it possible to write equilibrium expressions in which the swelled polymeric acids and anions behave *as though* they were dissolved species?

It seemed to us that the most staightforward way to investigate this problem would be to write equilibrium expressions for the proton-transfer reactions examined here, define equilibrium "constants" in the usual way, and then see if these K's do in fact remain constant as the total amounts of starting acid and base are varied.

By definition, the equilibrium constant for reaction between a polymer-bound acid and its polymer-bound conjugate anion, in the presence of a soluble acid and its soluble conjugate base (eq 4), is given by eq 5



$$\mathrm{AH} + \mathrm{B}^- \rightleftharpoons \mathrm{BH} + \mathrm{A}^- \qquad (4)$$

$$K_{\mathrm{eq}} = \frac{a_{\mathrm{BH}} a_{\mathrm{P\text{-}A^-}}}{a_{\mathrm{B^-}} a_{\mathrm{P\text{-}AH}}} \simeq \frac{[\mathrm{BH}]\{\mathrm{P\text{-}A^-}\}}{[\mathrm{B^-}]\{\mathrm{P\text{-}AH}\}} \qquad (5)$$

where the symbols in the first ratio represent activities. For dilute soluble systems, we would normally replace these activities by concentrations, and the K_{eq} so defined would remain constant over a wide range of initial concentrations of acid and base.[27] In our polymer systems, we define the concentrations of soluble species in the normal way, using conventional symbolism for these values. We define the "concentrations" of polymer-bound species as the ratio of the number of milliequivalents of polymer-attached acid or base in a given experiment to the number of milliliters of solvent used. Since these are not dissolved species, we use the modified brackets shown in eq 5 to represent these quantities.

We first examined the supported molybdenum hydride/soluble molybdenum anion system to determine whether it adhered to this equilibrium model. The data given in Table III were used to calculate a value of K for several different ratios of added soluble $CpMo(CO)_3Na$ to polymer-bound $CpMo(CO)_3H$ (see Experimental Section for the method of K_{eq} calculation). A plot of these K's vs. the ratio of soluble to bound molybdenum shows that they are in fact constant; i.e., the system adheres quite nicely to the equilibrium model. Constructing a similar plot using the data obtained with the lithium salt of the soluble anion also gives a constant K, with an average value very close to that obtained for the sodium salt (Figure 1).

This equilibrium was next approached from the opposite side. Data taken from experiments in which soluble hydride **6** was added to supported anion **P-7Na** (Table IV) were again used to construct a plot of K vs. the ratio of soluble Mo to supported Mo (Figure 1). Again a constant K was obtained, although the absolute value did not quite match that obtained from the experiments which started with soluble base and supported hydride. The equilibrium was also investigated using the supported lithium salt **P-7Li**. In this case, although still in agreement within an order of magnitude, the absolute value of K differed markedly from that observed in the first three plots. We believe that this is due to the fact that the polymer used to obtain the Li^+ data was prepared by a synthetic route different from that used to obtain the first three runs. The uncertainty in our measurement of the total amount of active molybdenum bound to the resin (vide supra) probably accounts for this difference in calculated values of K_{eq}.

Effective equilibrium constants were obtained for the reactions between Ⓟ-COOH and $CpMo(CO)_3Na$ (and its reverse reaction, Ⓟ-COONa and $CpMo(CO)_3H$) from the data of Table II. The calculated equilibrium constants are once again essentially constant at varying ratios of starting materials, and, within experimental error, the same K_{eq} is obtained starting for both sides of the equilibrium.

In conclusion, we have been able to demonstrate that proton-transfer equilibria between soluble and polymer-bound acids and bases can be effectively investigated, especially if the soluble components are quantitatively analyzable by IR spectroscopy. The reactions of the supported molecules studied behave analogously to reactions between soluble species, and seem to obey conventional equilibrium theory. Finally, although we do not feel that *absolute* pK_as of these species in THF are very meaningful, it is clear that the acidities of soluble $CpMo(CO)_3H$ and its polymer-bound analogue are very nearly identical, and that this conclusion also applies to the organic acid *p*-*i*-$C_3H_7C_6H_4COOH$ and its polymer-bound analogue.

Experimental Section

General. The 3% cross-linked macroreticular polystyrene–divinylbenzene copolymer was purified from industrial contaminants[5c] by stirring in the following solvents under the specified conditions: CH_2Cl_2, reagent grade, 25 °C, 2.5 h; THF, reagent grade, 50 °C, 2 h; H_2O, distilled, 70 °C, 2 h; HCl (aqueous), 1 M, 70 °C, 2 h; H_2O, distilled, 50 °C, overnight; KOH (aqueous), 1 M, 50 °C, 1 h; H_2O, distilled, 3 × 5 min; MeOH, reagent grade, 50 °C, 2 h; benzene, reagent grade, 55 °C, 2 h; benzene, purified, 55 °C, 2 h; CH_2Cl_2, purified, 55 °C, 2 h; Et_2O, anhydrous, 55 °C, 1 h. The beads were then dried overnight in vacuo.

The use of magnetic stirrers led to pulverization of the polymer beads. This was not considered disadvantageous since it was observed that diffusion rates of soluble reagents into internal polymer sites increased on reduced particle size. In addition, the IR bands of mulls of powdered resins were better resolved than those of mulls made from intact beads.

n-Butyllithium (2.2 M in hexane), methyllithium (1.45 M in diethyl ether), and lithium triethylborohydride (1 M in THF) were used as received. Tetramethylethylenediamine (TMEDA) was distilled from CaH_2 and degassed before use. 2-Cyclopentenone was distilled at reduced pressure immediately prior to its use. $Mo(CO)_6$ and $[MoCp(CO)_3]_2$ were used as received. NaH and LiH were rinsed free from mineral oil with hexane and stored in a inert atmosphere. *p*-Toluenesulfonic acid monohydrate was dehydrated by azeotropic distillation with benzene. Diethyl malonate, ethyl acetoacetate, 2-carboethoxycyclohexanone, and 2-carboethoxycyclopentanone were each fractionally distilled from molecular sieves (4 Å) at reduced pressure and degassed prior to use.

Tetrahydrofuran (THF), benzene, cyclohexane, diethyl ether, and 1,4-dioxane were vacuum transferred from sodium benzophenone ketyl and thoroughly degassed. Acetonitrile was distilled from P_2O_5 and thoroughly degassed.

Unless indicated otherwise, all reactions and routine manipulations were carried out at 20 °C under a nitrogen atmosphere in a drybox. Reactions requiring heating or cooling were performed on conventional vacuum lines using Schlenk techniques.

Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer, using the absorbance mode for quantitative analysis. Proton nuclear magnetic resonance spectra were recorded on a Varian EM-390 spectrometer.

Elemental analyses were performed by the University of California (Berkeley) Microchemical Analytical Laboratories. Metal analyses were performed by atomic absorption spectrometry on resin samples which had been digested in sulfuric acid and hydrogen peroxide.

Polymer-Bound Phenyllithium.[14a] Polystyrene resin (5 g, 47.6 mequiv in styrene monomer) was stirred in cyclohexane (30 mL) under argon at 50 °C for 1 h in a 300-mL Schlenk flask. To this stirring slurry, we added TMEDA (11.2 mL, 74.2 mmol) via syringe over 15 min, followed by a similar addition of *n*-BuLi (30 mL, 72.6 mmol) over 5 min. The beads rapidly changed from white to tan. The mixture was stirred at 65 °C for 7 h, during which time the cyclohexane solution changed from yellow to dark orange. The lithiated polymer was filtered under reduced pressure and washed with cyclohexane (6 × 30 mL) and THF (3 × 30 mL) until the washings were clear. The remaining salmon-colored beads were charged with THF (30 mL) for the following reaction with cyclopentanone.

Polymer-Bound Cyclopentadiene (P-3).[6b] To the stirring THF slurry of lithiated polystyrene from the previous reaction, cooled in an ice bath,

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(24) (a) A referee has indicated some concern about the fact that no direct information is available about the distribution of functionalities on the polymers discussed here. If we had observed that polymer attachment caused a dramatic change in the pK_a of the molybdenum hydride, site-aggregation effects would have to be considered as a possible explanation. However, the fact that little change in pK_a is produced upon polymer attachment makes it seem quite unlikely that site–site interaction, if it occurs, has a detectable effect on the acidity of the attached functional groups. Additional support for this point of view is provided by earlier work from Collman's group demonstrating that materials prepared by functionalization of preformed polymers are chemically very similar to those formed by polymerization of analogously functionalized monomers. Cf. (b) J. P. Collman, L. S. Hegedus, M. P. Cooke, J. R. Norton, G. Dolcetti, and D. N. Marquardt, *J. Am. Chem. Soc.*, **94**, 1789 (1972).

(25) (a) F. G. Bordwell et al., *J. Am. Chem. Soc.*, **97**, 7006 (1975); (b) H. W. Walker, C. T. Kresge, P. C. Ford, and R. G. Pearson, *ibid.*, **101**, 7428 (1979); (c) R. P. Bell, "The Proton in Chemistry", Cornell University Press, Ithaca, N.Y., 1959; (d) H. C. Brown, D. H. McDaniel, and O. Hafliger in "Determination of Organic Structures by Physical Methods", Vol. 1, E. A. Braude and F. C. Nachod, Eds., Academic Press, New York, 1955, p 588.

(26) We agree wholeheartedly with a referee's suggestion that an absolute value of the pK_a of $CpMo(CO)_3H$ in a solvent such as methanol (in which other hydride pK_as have recently been measured, cf. ref 25b) would be very useful in general. However, it would be somewhat risky to extrapolate such a value to THF, an aprotic solvent of substantially lower dielectric constant than methanol.

(27) Rys and Steingger, drawing on an analogy between the insoluble polymeric matrix and a solid surface, have applied Langmuir isotherm theory to an analysis of the acidic activity of a polysulfonated resin: P. Rys and W. J. Steinegger, *J. Am. Chem. Soc.*, **101**, 4801 (1979).

Table III. Equilibration of Ⓟ–$CpMo(CO)_3H$ with $CpMo(CO)_3^-Li^+$ and $CpMo(CO)_3^-Na^+$

	starting materials[a]					soluble components at equilibrium		
expt	resin	amt of resin mg	mequiv[b] of $CpMo(CO)_3H$ bound to resin	$CpMo(CO)_3^-Na^+$, mmol	$CpMo(CO)_3^-Li^+$, mmol	$CpMo(CO)_3^-Na^+$, mmol	$CpMo(CO)_3^-Li^+$, mmol	$CpMo(CO)_3H$, mmol
1	**P-6**	89	0.058	0.019		0.008		0.011
2[c]	**P-6**	89	0.058	0.030		0.015		0.015
3[c]	**P-6**	89	0.058	0.042		0.024		0.018
4[c]	**P-6**	89	0.058	0.063		0.040		0.023
5	**P-6**	101	0.066		0.018		0.007	0.011
6[d]	**P-6**	101	0.066		0.033		0.017	0.016
7[d]	**P-6**	101	0.066		0.047		0.026	0.021
8[d]	**P-6**	101	0.066		0.061		0.039	0.022
9[d]	**P-6**	101	0.066		0.087		0.066	0.021[e]

[a] In each case, 5 mL of THF was used as solvent. [b] Determined by elemental analysis of molybdenum on the resin. [c] Performed by adding sequential amounts of $CpMo(CO)_3^-Na^+$ to the equilibrated solution of the previous experiment. [d] Performed by adding sequential amounts of $CpMo(CO)_3^-Li^+$ to the equilibrated solution of the previous experiment. [e] Decrease in $CpMo(CO)_3H$ concentration from previous experiment is probably due to decomposition of the hydride in solution.

Table IV. Equilibration of Ⓟ–$CpMo(CO)_3^-Na^+$ and Ⓟ–$CpMo(CO)_3^-Li^+$ with $CpMo(CO)_3H$

		starting materials[a]				soluble components at equilibrium		
expt	resin	amt of resin, mg	mequiv[b] of $CpMo(CO)_3^-Na^+$ on resin	mequiv[c] of $CpMo(CO)_3^-Li^+$ on resin	$CpMo(CO)_3H$, mmol	$CpMo(CO)_3^-Na^+$, mmol	$CpMo(CO)_3^-Li^+$, mmol	$CpMo(CO)_3H$, mmol
1	**P-7**-Na	94	0.060		0.024 05	0.015 85		0.008 20
2[d]	**P-7**-Na	94	0.060		0.034 77	0.019 70		0.015 07
3[d]	**P-7**-Na	94	0.060		0.045 56	0.023 00		0.022 56
4[d]	**P-7**-Na	94	0.060		0.061 52	0.026 62		0.034 90
5[d]	**P-7**-Na	94	0.060		0.066 82	0.028 86		0.037 96
6	**P-7**-Li	100		0.0495	0.022 28		0.017 19	0.005 09
7[d]	**P-7**-Li	100		0.0495	0.035 45		0.023 00	0.012 45
8[d]	**P-7**-Li	100		0.0495	0.052 37		0.029 23	0.023 14
9[d]	**P-7**-Li	100		0.0495	0.072 25		0.035 59	0.036 66

[a] In each case, 5 mL of THF was used as solvent. [b] Determined from elemental analysis of sodium on the resin, **P-7**-Na. [c] Determined from elemental analysis of lithium on the resin, **P-7**-Li. [d] Performed by adding sequential amounts of $CpMo(CO)_3H$ to equilibrated solution of previous experiment.

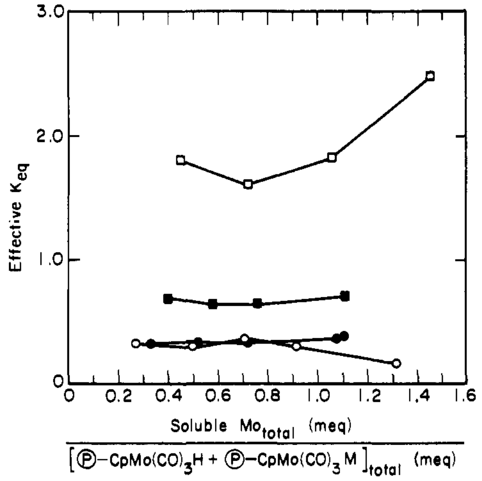

Figure 1. Equilibrium constants plotted as a function of the molar ratios of soluble to polymer-bound components of equilibrium mixtures. The equilibrium mixtures result from combination of (a) Ⓟ$Cp\text{-}Mo(CO)_3H$ and $CpMo(CO)_3Li$ (○); (b) Ⓟ-$CpMo(CO)_3H$ and $CpMo(CO)_3Na$ (●); (c) Ⓟ-$CpMo(CO)_3Li$ and $CpMo(CO)_3H$ (□); (d) Ⓟ-$CpMo(CO)_3Na$ and $CpMo(CO)_3H$ (■).

was added cyclopentenone (9 mL, 108 mmol) via syringe over 4 min. The beads turned from pink to yellow and then to white over the course of the addition. After stirring under argon for 12 h, the cyclopentadienyl polymer was filtered under positive argon pressure and washed with the following solvents: THF (2 × 30 mL); THF-H_2O (1:1, 2 × 30 mL); H_2O (30 mL) (beads changed from light yellow to white); MeOH (2 × 30 mL); benzene (3 × 30 mL). The resulting polymer was dried in vacuo at 40 °C. A weight gain of 1.18 g was recorded corresponding to a 38% substitution of styrene monomers by cyclopentadiene, or 2.95 mequiv of cyclopentadiene/g of cyclopentadienyl polymer. Elemental analysis for lithium on a sample of cyclopentadienyl resin (**P-3**) which had been previously treated with methyllithium[6b] agreed well with the cyclopentadienyl substitution percentages derived from weight-gain calculations. The resinolithium cyclopentadienide was prepared by adding to a slurry of polymer-bound cyclopentadiene (**P-3**) in THF a diethyl ether solution of methyllithium (fivefold excess), whereupon bubbling was observed (presumably methane). After 4 h the resulting light pink polymer was washed with diethyl ether and THF and dried in vacuo.

The degree of cyclopentadiene substitution on the polystyryl resin derived from the above two methods agreed with a third analysis performed by titration of resin **P-3**. A standardized THF solution of sodium triphenylmethide, prepared by reaction of $NaNH_2$ with triphenylmethane, was added slowly from a buret to a stirring THF slurry of **P-3** over 12 h. The red color of sodium triphenylmethide served as an end-point indicator. The titration required the lengthy term to assure equilibration with all internal polymeric sites.

$Mo(CO)_3(CH_3CN)_3$. The procedure described in the literature[28] was followed. The reaction was monitored by IR for disappearance of $Mo(CO)_6$ (1980 cm^{-1} (THF)) over 2 days, after which time the solvent (CH_3CN) was removed at reduced pressure, leaving a light yellow, powdery residue.

Reaction of Polymer-Bound Cyclopentadiene (P-3) with $Mo(CO)_3(CH_3CN)_3$. In a representative synthesis of resin **P-4**, a slurry of polymer-bound cyclopentadiene (**P-3**, 1.15 g, ~3.4 mequiv in Cp in THF (40 mL) was combined with an excess of $Mo(CO)_3(MeCN)_3$ (3 g, 9.9 mmol) and the mixture was stirred at 70 °C under argon for 12 h. The resulting beads, red after extensive washing in THF and drying in vacuo, exhibited infrared bands at 2025 (m), 1948 (s, br), and 1902 (s) cm^{-1} (KBr). Such a pattern of bands corresponds to a mixture of monomers of $MoCp(CO)_3H$ (2006 (m), 1883 (s, br) cm^{-1} (KBr)) and $(MoCp(CO)_3)_2$ (1900 (s), 1950 (s) cm^{-1} (KBr)). The red color of the resulting beads also implicates the formation of dimeric ($[RCp(CO)_3Mo]_2$) groups on the polymer. Elemental analysis of this molybdenum resin **P-4** showed ap-

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[28] S. A. Keppie and M. F. Lappert, *J. Organomet. Chem.*, **19**, P5 (1969).

proximately 0.8 mequiv of molybdenum/g of polymer (7.77% Mo). This corresponds to approximately 31% of the cyclopentadienyl ligands on the resin being bound to molybdenum.

Reaction of Molybdenum Resin P-4 with $HB(C_2H_5)_3Li$. Resin **P-4** (0.75 g, ~0.6 mequiv Mo), containing a mixture of bound $CpMo(CO)_3H$ and bound $[CpMo(CO)_3]_2$, was swelled in THF (10 mL) for 1 h. Immediately on addition of $HB(C_2H_5)_3Li$ (3.0 mL of a 1 M THF solution, 3 mmol), a change in the resin's color from red to brown was accompanied by vigorous gas evolution. The resin was stirred for 5 h, filtered, washed with THF, and dried in vacuo. The resulting beige polymer **P-5** exhibited IR absorption at 1898 (s), 1773 (s), and 1703 (s) cm^{-1} (KBr), characteristic of $RCpMo(CO)_3^-Li^+$.

Ⓟ-$CpMo(CO)_3H$ (P-6). In a representative acidification of **P-5**, **P-5** (3.21 g, ~2.6 mmol Mo) was swelled in THF (40 mL) over 1 h. *p*-Toluenesulfonic acid (0.50 g, 2.75 mmol) in THF (20 mL) was added over several hours from an addition funnel to the stirring polymer slurry. After an additional 6 h of stirring, an aliquot of the reaction solvent was tested with an indicator for residual acidity to assure that an excess of protonating reagent had been used. On confirmation of acidity, the slurry was extensively washed with clean THF until the rinses, in contact with the resin for at least 1 h, contained no further acid. The resulting beige resin **P-6** was then dried in vacuo. Infrared absorbances for **P-6** are given in Table I. Elemental analysis was performed on its sodium derivative **P-7Na** (cf. next section).

Ⓟ-$CpMo(CO)_3^-M^+$ (P-7). In a representative synthesis of polymer-bound molybdenum anion (**P-7**), polymer-bound molybdenum hydride (2.86 g, ~1.86 mmol Mo) was swelled in THF (20 mL) for 1 h. Monosodium diethyl malonate (vide infra) (6.59 mmol in 35 mL of THF) was added from an addition funnel to the stirring resin over several hours. After an additional 6 h of stirring, the reaction solvent was checked by IR for residual sodium diethyl malonate to assure that an excess of the deprotonating reagent had been used. The resin was then extensively washed with clean THF until rinses, in contact with the resin for at least 1 h, concentrated on a rotary evaporator, and checked by IR, contained no detectable diethyl malonate or its sodium salt. The resulting light beige resin **P-7Na** was dried in vacuo. IR absorbances for **P-7Na** are given in Table I. Elemental analysis of **P-7Na** gave a molybdenum content of 0.74 mmol of Mo/g of polymer, slightly higher than that for sodium of 0.64 mmol of Na/g of polymer (Mo, 7.08%; Na, 1.47%). The lithium salt of polymer-bound molybdenum anion **P-7Li** was prepared in an analogous manner using monolithium diethyl malonate as a base. Elemental analysis of resin **P-7Li** yields 0.67 mmol of Mo and 0.49 mmol of Li/g of polymer (Mo, 6.43%; Li, 0.34%). IR absorbances of resin **P-7Li** are given in Table I.

Polymer-Bound Organic Carboxylates. Ⓟ-C_6H_4COOH (P-1).[14] Polymer-bound phenyllithium (3 g) was prepared as described above, charged with THF (75 mL), cooled to −78 °C, and evacuated. Carbon dioxide was introduced to the THF solution of resinophenyllithium in the following manner. A 300-mL flask of dry ice, connected to a vacuum manifold, was subjected to several freeze–pump–thaw cycles to remove oxygen. The flask was then allowed to warm to room temperature; gaseous CO_2 boil-off was passed through a column of activated molecular sieves (4 Å) and bubbled into the THF resin slurry (now at ambient temperature) via a gas dispersion stick. The color of the resin quickly changed from pink to white. The positive pressure in the manifold was monitored with a mercury bubbler, an increase in pressure (i.e., a decrease in CO_2 uptake by the resin) indicating completion of the reaction. After 15 min the CO_2 uptake was negligible; however, the bubbling was continued for an additional 2 h to assure exposure of all internal polymeric sites to the CO_2. In the air, the resin was worked up according to the method of Fyles and Leznoff[14b] and the resulting resin **P-1** was dried in vacuo. The degree of carboxylic functionalization was determined by titration (next section). The infrared carbonyl absorptions of carboxylic acid resin **P-1** are given in Table I.

Ⓟ-C_6H_4COONa (P-2). Polymeric sodium benzoate was prepared by titration of Ⓟ-C_6H_4COOH (**P-1**) with sodium hydroxide. Direct titration of the polymeric carboxylic acid with the alkaline titrant was tedious because of slow diffusion rates of reactants into the polymer. For this reason the following back-titration method was employed (in this case no precautions were taken to exclude air). The aqueous NaOH titrant (0.09 M) was standardized against primary standard potassium acid phthalate. The aqueous HCl titrant (0.11 M) was standardized against primary standard sodium carbonate. Phenolphthalein and bromophenol blue were used as indicators in titrations for acid and base, respectively. In a typical titration, 100 mg of polycarboxylic resin **P-1** was placed in a flask equipped with a magnetic stir bar and allowed to swell in THF or 1,4-dioxane (10 mL) for ~1 h. An amount of alkaline titrant corresponding to a slight excess relative to the estimated number of acidic polymeric sites was then added all at once. The slurry was allowed to equilibrate with stirring overnight. The total solution was then back-titrated with the acid titrant, using standard buret techniques, until an end point was reached. The loading of carboxylic acid sites on the polymer **P-1**, calculated from the net amount of base "consumed" by the resin, was found to be 2.32 ± 0.06 mequiv of H^+/g of Ⓟ-COOH(**P-1**). Unreasonably low results for carboxylate functionalization were obtained when the resin **P-1** was not preswelled in the *organic* solvent. This is presumably due to the inaccessibility of internal polymer sites which rely on solvation by a relatively nonpolar solvent for exposure to external reagents.[16] The volume of organic solvent had to be at least that of the total aqueous titrant introduced during the titration. Infrared absorptions for Ⓟ-C_6H_4COONa (**P-2**) are given in Table I.

Alkali Metal Salts of β-Dicarbonyl Compounds. Diethyl malonate, ethyl acetoacetate, 2-carboethoxycyclopentanone, and 2-carboethoxycyclohexanone were converted to their monosodium salts in the following manner. A THF solution (~0.3 M) of the β-dicarbonyl was added from an addition funnel to a stirred slurry of a slight excess of NaH in THF (of approximately equal volume) over 1 h. Rapid gas evolution was observed. The resulting solution, checked by IR for complete conversion to the monosodium salt, was decanted from residual NaH and treated as follows. When the β-dicarbonyl sodium salts were to be used in excess as a synthetic reagent (e.g., in the conversion of **P-6** to **P-7**), the salts were used in situ in their THF solutions. However, when the β-dicarbonyl salts were to be used to carefully monitor proton-transfer activity of polymeric hydride **P-6**, they were first purified by crystallization. After the removal of THF at reduced pressure the following anhydrous cyrstallizing solvents were employed for each salt: sodium diethyl malonate, hot methylene chloride; sodium ethyl acetoacetate, hot diethyl ether; sodium 2-carboethoxycyclopentanone, ethanol; sodium 2-carboethoxycyclohexanone, ethanol. Infrared carbonyl absorbances in THF for each β-dicarbonyl and its conjugate base were as follows: diethyl malonate, 1750, 1735 cm^{-1}; sodium salt, 1670, 1550 cm^{-1}; lithium salt, 1660, 1530 cm^{-1}; ethyl acetoacetate, 1745, 1720 cm^{-1}; sodium salt, 1660, 1510 cm^{-1}; 2-carboethoxycyclopentanone, 1760, 1735 cm^{-1}; sodium salt, 1665, 1515 cm^{-1}; 2-carboethoxycyclohexanone, 1745, 1717 cm^{-1}; sodium salt, 1660, 1483 cm^{-1}. The lithium salt of diethyl malonate was prepared as above, except that LiH was substituted for NaH.

Monomeric Molybdenum Compounds. $CpMo(CO)_3H$ (**6**), $CpMo(CO)^-Na^+$ (**7-Na**), and $CpMo(CO)_3CH_3$ (**8**) were synthesized according to literature methods.[29] $CpMo(CO)_3^-Na^+$ was also synthesized by substituting $NaBH_4$ for sodium amalgam in the literature procedure. Infrared spectral data are given in Table I.

$CpMo(CO)_3^-Li^+$ (7-Li).[19] To a stirring solution of $[CpMo(CO)_3]_2$ (2.0 g, 4.08 mmol) in THF (10 mL) was added $HB(C_2H_5)_3Li$ (15 mL of a 1.0 M THF solution, 15 mmol) from an addition funnel over 10 min. The solution changed from red to brown over the course of the addition; an infrared spectrum immediately following the addition indicated that the reduction was complete. Solvent was removed under reduced pressure and the lithium salt was crystallized from diethyl ether–benzene, yield 1.98 g (75%). Infrared data are given in Table II. The NMR spectrum of **7-Li** indicates that one molecule of THF is incorporated into the crystal of $CpMo(CO)_3^-Li^+$ (^1H NMR (acetone-d_6) δ 4.93 (s, C_5H_5, 5 H), 3.60 (s, THF, 4 H), 1.79 (s, THF, 4 H)).

Beer's Law Determination of Extinction Coefficients. Standard procedures for deriving Beer's law plots were followed. Plots of ϵ vs. concentration covered the concentration range in which equilibration experiments were to be run: 0.01–0.11 M for organic carbonyl compounds and 0.001–0.015 M for transition metal carbonyl compounds. All extinction-coefficient determinations (and subsequent equilibration reactions) were carried out in THF, typically in a 5- or 10-mL volumetric flask equipped with a magnetic stir bar. Infrared spectra were recorded in absorbance units. An electronic expansion feature on the IR spectrophotometer was employed for solutions of low concentrations. Each spectrum was recorded five times, yielding an averaged peak height for each band from the five scans at each concentration. Extinction coefficients for the carbonyl bands of the following compounds were determined [compound, CO wavenumber in cm^{-1} (extinction coefficient, ϵ)]: $CpMo(CO)_3H$, 2015 (3.20×10^3), 1932 (5.55×10^3); $CpMo(CO)_3^-Na^+$, 1903 (4.18×10^3), 1798 (4.50×10^3), 1745 (3.13×10^3); $CpMo(CO)_3^-Li^+$, 1910 (2.50×10^3), 1810 (3.10×10^3), 1785 (1.0×10^3), 1718 (2.45×10^3); diethyl malonate, 1750 (5.96×10^2), 1735 (7.01×10^2); sodium diethyl malonate, 1673 (1.67×10^3), 1550 (1.11×10^3).

Equilibration Reactions. Equilibria between polymer-bound and soluble species were set up and monitored as described earlier. Reactions between bound acids and soluble species of similar pK_a were monitored in the same manner (by IR) as reactions between bound acids and substrates of greatly differing acidity (e.g., the reactions between Ⓟ-

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(29) P. L. Watson and R. G. Bergman, *J. Am. Chem. Soc.*, **101**, 2055 (1979), and ref 4 cited therein.

$CpMo(CO)_3H$ (**P-6**) and the β-dicarbonyl sodium salts). The former followed weak acid–weak base behavior and the latter behaved essentially as an acid-exchange resin.

"Effective K_{ea}" Calculations. The numbers for eq 5 were supplied in the following manner. The concentrations of soluble species, $[B^-]$ and [BH], were calculated directly from IR absorbances using Beer's law and the above-determined extinction coefficients. The effective concentration of Ⓟ-A^-, {Ⓟ-A^-}, was assumed to be equal to that of BH, in accordance with eq 4. {Ⓟ-AH} was then determined from the difference between {Ⓟ-AH}$_{initial}$ and {Ⓟ-A^-}. For example, K_{eq} for experiment 1 of Table III would be calculated as follows:

$$K_{eq} = \frac{[BH]\{P\text{-}A^-\}}{[B^-]\{P\text{-}AH\}} = \frac{(0.011)(0.011)}{(0.008)(0.058 - 0.011)} = 0.32$$

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Anomalous Spin Hamiltonian Parameters of Pseudotetrahedral Copper(II) Complexes. ESR Spectra of Copper(II)-Doped Dichlorobis(triphenylphosphine oxide)zinc(II)

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Abstract: The X-band (9 GHz) ESR spectra of the copper(II)-doped pseudotetrahedral complex dichlorobis(triphenylphosphine oxide)zinc(II) have been recorded on single crystal at 4.2 K. They are interpreted by using the spin Hamiltonian parameters $g_1 = 2.46$, $g_2 = 2.08$, $g_3 = 2.08$, $A_1 = 40 \times 10^{-4}$ cm^{-1}, $A_2 = 25 \times 10^{-4}$ cm^{-1}, $A_3 = 20 \times 10^{-4}$ cm^{-1}. The superhyperfine interaction of the unpaired electron with two equivalent chlorine atoms is also observed. The Q-band (35 GHz) ESR spectra have been recorded at 77 K, yielding $g_1 = 2.43$, $g_2 = 2.09$, and $g_3 = 2.08$. The difference in the g_1 values of the pure and the copper-doped zinc complex is related to structural differences between the copper and zinc lattices. A model including the spin–orbit coupling interaction of the unpaired electron with the ligands is proposed which rationalizes the spin Hamiltonian parameters of $CuCl_4$ and CuX_2Cl_2 pseudotetrahedral chromophores. The anomalously low $A_{\parallel}$ values seen in the ESR spectra of some sulfur-containing copper proteins are related to the covalency of the copper(II)–sulfur bonds.

Pseudotetrahedral copper(II) complexes are far less numerous than the square-planar ones. However they are attracting a large interest since tetrahedral copper(II) chromophores are known to be present in some metalloenzymes and metalloproteins.[1]

The ESR spectra are a powerful tool for the diagnosis of the coordination geometry of copper(II),[2] and as such they have been widely used also for tetrahedral complexes.[3] However their interpretation[4] still is controversial, and not all their features are fully understood.

The main differences seen in the ESR spectra of tetrahedral complexes as compared to the square-planar ones are as follows: (i) both $g_{\parallel}$ and $g_{\perp}$ are larger in tetrahedral complexes; (ii) $A_{\parallel}$ tends to be smaller in the tetrahedral chromophores, while less safe conclusions can be drawn for $A_{\perp}$. An elegant demonstration of this trend has been provided by Bertini et al.,[5] who reported the ESR spectra of copper(II)-dopedZinc(II) and nickel(II) salicylaldiminates, following the variation of the spin Hamiltonian parameters on passing from the tetrahedral to the square-planar chromophores present in the two lattices.

Recently also Marks and Ibers[6] shortly reviewed the main factors influencing the g and A values in four-coordinate copper(II) complexes.[7-10]

The above trends in the values of g are qualitatively well understood, in the sense that the g values must increase on passing from the square-planar to the tetrahedral structures since the energy separation of the electronic levels decreases. The same effect is expected to cause also a decrease of the $A_{\parallel}$ value, so that nothing mysterious seems to be operative, at least at the qualitative level. As a matter of fact there is a large class of tetrahedral copper(II) complexes whose $A_{\parallel}$ values can be reasonably well reproduced with usual formulas. Matters are different in the case of Cs_2CuCl_4, for which $A_{\parallel}$ as small as 25×10^{-4} cm^{-1} has been reported.[11-13] Sharnoff[12] studied thoroughly the system and suggested that the observed g and A values beared the contribution due to the admixture of the metal 4p orbitals in the ground level,[14] allowed by lack of an inversion center on the molecule. In order to reproduce the experimental values, however, he had to include a contribution as high as 13% of the 4p orbitals in the ground level.

Against this interpretation stands the fact that the mixing coefficient seems to be large and that no such large contribution is required in the interpretation of the ESR parameters of other tetrahedral[15] or trigonal-bipyramidal[16] copper(II) complexes, which also lack a center of symmetry.

With the aim to obtain new experimental data on complexes as similar as possible to $CuCl_4{}^{2-}$, we have now recorded the ESR spectra of copper(II)-doped $Zn(Ph_3PO)_2Cl_2$ (Ph_3PO = triphenylphosphine oxide). The analysis of these new data allowed us to suggest an alternative mechanism for the decrease of the $A_{\parallel}$ values observed in these complexes, which may be relevant to the interpretation of the ESR spectra of metalloenzymes and metalloproteins.

Experimental Section

$Zn(Ph_3PO)_2Cl_2$ and $Cu(Ph_3PO)_2Cl_2$ were prepared as previously reported.[17] Single crystals of both the pure copper and the copper-doped

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