Table I. Lithium Ion Pair p*K* of Lithium 1-Naphthylacetate, **2**, in THF at 25 °C

entry	10^3[**2**][a]	10^4[**3**][a]	p*K*[b]
A	1.38	0.648	22.13
B	2.25	0.642	22.05
C	1.38	0.738	22.12
D	2.50	0.821	21.97
E	4.02	3.02	21.83
F	3.59	3.16	21.82
G	4.65	4.08	21.76
H	2.90	5.71	21.73
I	3.77	6.38	21.74
J	3.39	9.36	21.66
K	2.75	11.6	21.66
L	2.33	11.4	21.62
M	5.20	14.5	21.65
N	2.44	15.6	21.45
O	3.07	17.3	21.54
P	10.6	8.22	21.99
Q	12.3	6.29	22.12
R	14.4	2.00	22.70

[a] Concentrations in M. [b] Measurements A, C, L, N, O against 9-*n*-butylfluorene (BuFl), p*K* = 22.36 (Gronert, S.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 2836). Measurements B, D–F, I–K, M, P–R against 9-benzyl-9-*H*-benzo[*def*]fluorene (BnMP), p*K* = 21.35.[19] Measurement G against 9-benzylfluorene (9-BnFl), p*K* = 21.36.[19]

alation of the parent acid with 2 equiv of a strong bulky base, such as lithium diisopropylamide, and allow facile synthesis of useful and unusual acid derivatives such as α-hydroperoxy acids,[10] highly substituted diacids,[14] β-keto acids,[6] and lactones.[12] Although the metal salts of carboxylic acid dianions are widely used in synthesis, little is known about their solution structure and stability. A computed structure is available for monomeric lithium lithioacetate,[15] but Bauer and Seebach[16] have shown that the dilithio salt of a model carboxylic acid is present as an aggregate in tetrahydrofuran (THF) at −108 °C. NMR studies of the dilithio salts of arylacetic acids indicate that much of the negative charge is localized on the oxygens, and therefore resonance from **1** is important.[17] We have shown previously that related ion-triplet

$$\underset{\mathbf{1}}{\mathrm{RCH{=}CO_2{}^{2-}\text{-}2Li^+}}$$

structures have enhanced coulombic stability.[18] We report a study of the ion pair acidity of such salts that makes use of our previously established lithium scale in THF.[19]

Initial studies with fluorene-9-carboxylic acid showed that its second ion pair p*K* was too low for the present scale; it is estimated as <13 because 1,3-diphenylindene failed to quench its dianion.[20,21] Considering that fluorene has an ion pair of p*K* of 22.75,[21,22] the CO_2Li group has an acidifying effect of at least 10 p*K* units. Further studies were made with the 1-naphthylacetic acid system because its salts have the necessary solubilities, spectra, and equilibration rates. In THF, lithium 1-naphthylacetate, **2**, is colorless, but the dilithium salt **3** has a visible absorbance at 442 nm (ϵ = 10 400). Table I summarizes the p*K* measurements with three indicators. The variation of the p*K* values demonstrates that the observed p*K* is dependent on the concentrations of the salts.[21] At higher dilithio salt concentrations, lower p*K* values are observed (entries A–O), and at higher monolithio salt concentrations, higher p*K* values are observed (entries E–J and P–R). This type of concentration dependence is consistent with both the mono- and dilithio salts being present as aggregates in THF.

If the average aggregations are effectively constant as $(\mathbf{2})_n$ and $(\mathbf{3})_m$, eq 1 may be derived based on an earlier analysis[21]

$$\log K_{\mathrm{obsd}} = [(m - 1)/m] \log [\mathbf{3}] + [(1 - n)/n] \log [\mathbf{2}] + C \qquad (1)$$

in which K_{obsd} = [**3**][IndH]/[**2**][Ind-Li]. This three-parameter equation gives values of approximately 2 and 3 for *m* and *n*, the average aggregation numbers for **3** and **2**, respectively. The analysis is oversimplified because it does not account for mixtures of aggregate types (dimer ⇄ tetramer) or mixed aggregates (**2·3**). Accordingly, the fit is only fair (residuals of about 0.1–0.2 p*K* units). Nevertheless, it does show that aggregates are involved and that the derived "p*K*" values should be regarded only as "effective p*Ks*" valid only for the concentration regions measured. This aspect of acidity measurements, namely that the acidities involving aggregated species are concentration dependent, is often neglected and should be given wider recognition.

The resulting effective acidity of the lithium carboxylate is remarkably high. Comparison with the corresponding ester would be instructive, but the p*K* of a naphthylacetate ester is not yet available; however, the p*K* of *tert*-butyl phenylacetate on the same lithium ion pair scale is 18.7.[22,23] Substitution of the α-naphthyl for the phenyl group should not change this value by more than 1–2 p*K* units.[24] Thus, the effective p*K* of the lithium salt, which involves aggregates and to which aggregation energies undoubtedly contribute significantly, is only a few units higher than that of a corresponding ester in which only monomers are involved; that is, the aggregated $-CO_2Li$ substituent provides nearly as much carbanion ion pair stabilization as the common acidifying substituents, $-CO_2R$, $-CN$, and $-SO_2R$.[23]

Acknowledgment. This research was supported in part by NSF Grants No. CHE 85-02137 and No. 87-21134. S.G. was an industrial fellow for 1986–1987 supported by the W. R. Grace Co.

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Synthesis of $(PCy_3)_2Cr(CO)_3$ and Its Reactions with Hydrogen, Nitrogen, and Other Ligands

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Received December 18, 1987

The recent discovery by Kubas and co-workers of the complexes $M(CO)_3(PR_3)_2$ (M = Mo, W, R = C_6H_{11}, *i*-C_3H_7) was of special significance since they were the first complexes shown to bind molecular hydrogen.[1] These complexes are readily prepared from the cycloheptatriene tricarbonyl complexes as shown in eq 1 below.

(1)

Attempts to prepare the chromium analogue of these complexes by the method shown in eq 1 have been unsuccessful. Isolable coordinatively unsaturated complexes are rare, especially for

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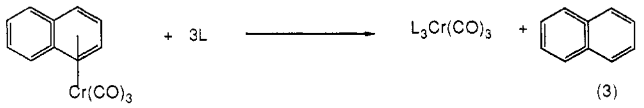
first-row metals. To our knowledge, none has been reported for chromium.[2]

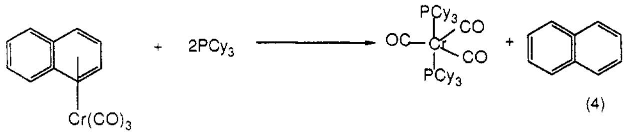
In view of calorimetric results for molybdenum[3] it seemed possible that failure to observe reaction 1 for chromium could be due to thermodynamic factors rather than inherent instability of $(PCy_3)_2Cr(CO)_3$. Thus the free energy of reaction 1 can be estimated to be only about −4 kcal/mol for molybdenum.[4] There is reason to anticipate that reaction 1 could be thermodynamically less favorable for chromium than for molybdenum and tungsten. The order of M–CO bond strengths has recently been shown to be Cr < Mo < W in the gas phase.[5] This appears to be generally true for the M–L bond in solution.[6] A consequence of this is that ligand substitutions are generally more exothermic for molybdenum and tungsten than for chromium. Since the unfavorable entropic component of reaction 1 should not change much as a function of M, reduction in the enthalpy of reaction would lead to a net positive free energy of eq 1 for chromium.

We have recently investigated the enthalpies of reactions 2 and 3 below. The reactions of the naphthalene complex are about 10 kcal/mol more exothermic than analogous reactions of the cycloheptatriene complex.[6] It seemed possible that this might provide the additional driving force necessary for formation of the previously unknown chromium complex shown in eq 4. In diethyl ether or THF at room temperature, reaction 4 proceeds in high yield to give the dark blue crystalline complex $(PCy_3)_2Cr(CO)_3$.

(2)

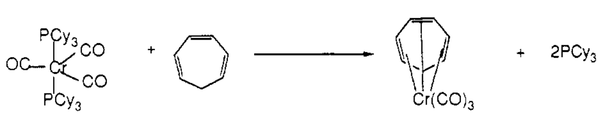


(3)



(4)

Failure to produce this complex via reaction 1 is, in fact, due to thermodynamic control. The reverse reaction occurs quantitatively at room temperature as shown in eq 5. This is an unusual reaction, we are not aware of a similar case where a polyolefin displaces phosphine ligands. The driving force for reaction 5 is the favorable entropy of reaction since two moles of phosphine are displaced by cycloheptatriene. The discovery of reactions 4 and 5 were a direct outcome of previous thermochemical results and simple estimates made from them.



(5)

Having prepared $(PCy_3)_2Cr(CO)_3$ it was of interest to see if the chromium complex would bind molecular hydrogen, nitrogen, and other ligands in analogy to the molybdenum and tungsten complexes. There are few molecular hydrogen complexes of first-row metals.[1] It has been shown that photochemically generated $Cr(CO)_5$ will bind hydrogen in a matrix and has fleeting existance at room temperature.[7] Unlike the molybdenum and tungsten analogues, at room temperature and pressure the complex $(PCy_3)_2Cr(CO)_3$ shows *no* tendency to bind either hydrogen or nitrogen. Stronger ligands such as acetonitrile, pyridine, $P(OMe)_3$, and CO form stable complexes as shown in reaction 7. Infrared data for these complexes are shown in Table I along with data for the analogous Mo and W complexes. The ligands are not as tightly bound in the Cr system. For example, pyridine which binds quantitatively for the Mo and W complexes[1] partially dissociates in solution as shown in eq 8 below. This is in keeping with the reduced bond strengths expected for first-row complexes.

$$Cr(CO)_6 \xrightarrow{h\nu} CO + Cr(CO)_5 \xrightarrow{H_2} Cr(CO)_5(H_2) \qquad (6)$$

$$(PCy_3)_2Cr(CO)_3 + L \rightarrow (PCy_3)_2Cr(CO)_3(L) \qquad (7)$$

$$L = CH_3CN,\ py,\ P(OMe)_3,\ CO$$

$$(PCy_3)_2Cr(CO)_3(py) \rightleftharpoons (PCy_3)_2Cr(CO)_3 + py \qquad (8)$$

The observed lack of binding of nitrogen and hydrogen at room temperature and pressure is also due to thermodynamic factors. Ligand addition reactions such as that shown in eq 8 must be exothermic enough to overcome an unfavorable entropy term on

Table I. Infrared Data[a] for the Complexes $(PCy_3)_2M(CO)_3(L)$

L =	Cr	Mo	W
	1935 w	1952 w	1945 w
	1821 s	1840 s	1829 s
	1809 m	1809 m	1807 m
		2695 w[b]	2641 w[b]
H_2	1947 w	1961 w	1958 w
	1836 s	1850 s	1840 s
N_2	1940 w	1955 w	1948 w
	1843 s	1853 s	1846 s
	2128 w[c]	2147 w[c]	2113 w[c]
CH_3CN	1924 w	1940 w	1933 w
	1813 s	1826 s	1817 s
		1809 sh	
pyridine	1907 w	1933 w	1925 w
	1795 s	1812 s	1802 s
$P(OMe)_3$	1937 w	1952 w	1947 w
	1842 m	1852 m	1849 m
	1821 s	1834 s	1826 s
CO	1856 vs	1866 vs	1859 vs

[a] Solution spectra (cm^{-1}) run at room temperature in toluene. For data in Nujol mulls on some of the Mo and W complexes see ref 1. [b] The C–H stretch of the hydrogens bound to the metal through the three-center M···H–C bond, absent for Cr. [c] Stretching frequency for the bound N_2.

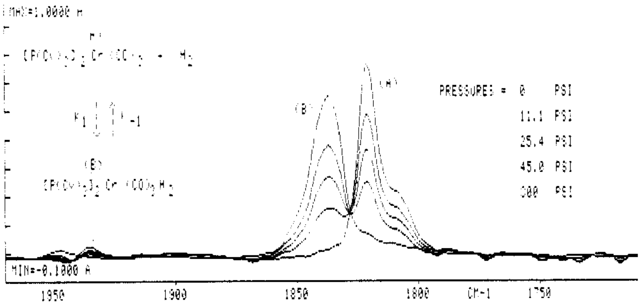


Figure 1. Infrared spectra of $(PCy_3)_2Cr(CO)_3$ under various pressures of H_2. The peak at 1821 cm^{-1} due to $(PCy_3)_2Cr(CO)_3$ decreases as the band at 1836 cm^{-1} due to $(PCy_3)_2Cr(CO)_3(H_2)$ increases. Spectra run at 25.0 °C in toluene.

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(2) We are not aware of a 16-electron complex reported for chromium. The 17-electron complex $Cr(CO)_2(PPh_3)(C_5H_5)$ has been reported [Cooley, N. A.; Watson, K. A.; Fortier, S.; Baird, M. C. *Organometallics* **1986**, *5*, 2563.

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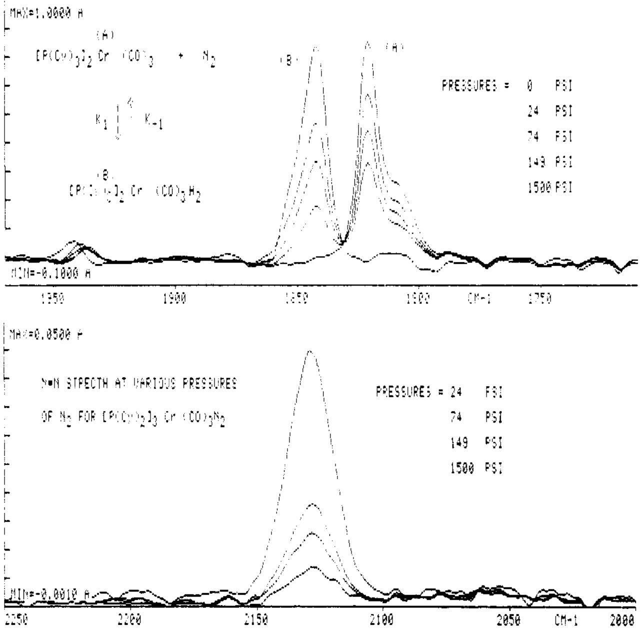

Figure 2. Infrared spectra of $(PCy_3)_2Cr(CO)_3$ under various pressures of N_2. The band at 1821 cm^{-1} due to $(PCy_3)_2Cr(CO)_3$ decreases as the band at 1843 cm^{-1} increases. The bottom figure shows the absorbance (scale expanded 20×) at 2128 cm^{-1} due to the N_2 stretch. Spectra run at 25.0 °C in toluene.

the order of 10 kcal/mol.[4b] Since the Cr–L bond is generally weaker than analogous Mo–L and W–L bonds, the hydrogen and nitrogen complexes fall below this and have net unfavorable free energies of formation. Either lowering the temperature or raising the pressure allows spectroscopic observation of the molecular hydrogen and nitrogen complexes. Infrared spectra of the reversible binding of hydrogen and nitrogen as a function of pressure are shown in Figures 1 and 2.

$$(PCy_3)_2Cr(CO)_3 + H_2 \rightleftharpoons (PCy_3)_2Cr(CO)_3(H_2) \qquad (9)$$

$$(PCy_3)_2Cr(CO)_3 + N_2 \rightleftharpoons (PCy_3)_2Cr(CO)_3(N_2) \qquad (10)$$

The chromium complex bears strong resemblence to the molybdenum and tungsten analogues; however, it also shows some important differences. Equilibrium data[6] indicate that it binds hydrogen more strongly than nitrogen, the opposite of behavior for the molybdenum and tungsten analogues. This is clearly shown in Figures 1 and 2 where higher pressures are needed to form the dinitrogen complex.

The preparation of this complex completes the series $(PCy_3)_2M(CO)_3$, M = Cr, Mo, W. There are few isolable complexes of this type known, and we are not aware of any which spans a complete triad of metals. This provides a good opportunity to investigate in detail the role of the metal in determining metal-ligand bond strengths in solution. Additional kinetic and thermodynamic studies on these and related complexes are in progress.

Acknowledgment. Support of this work by the National Science Foundation (Grant CHE-8618753) is gratefully acknowledged.

Registry No. $(PCy_3)_2Cr(CO)_3$, 114595-36-7; $(PCy_3)_2Cr(CO)_3(H_2)$, 114595-37-8; $(PCy_3)_2Cr(CO)_3(N_2)$, 114595-38-9; $(PCy_3)_2Cr(CO)_3(CH_3CN)$, 114595-39-0; $(PCy_3)_2Cr(CO)_3(py)$, 114595-40-3; $(PCy_3)_2Cr(CO)_3[P(OMe)_3]$, 114595-41-4; $(PCy_3)_2Cr(CO)_4$, 20957-94-2; $(PCy_3)_2Mo(CO)_3$, 73690-53-6; $(PCy_3)_2Mo(CO)_3(H_2)$, 104198-76-7; $(PCy_3)_2Mo(CO)_3(N_2)$, 73690-54-7; $(PCy_3)_2Mo(CO)_3(CH_3CN)$, 100995-28-6; $(PCy_3)_2Mo(CO)_3(py)$, 100995-30-0; $(PCy_3)_2Mo(CO)_3[P(OMe)_3]$, 114595-42-5; $(PCy_3)_2Mo(CO)_4$, 54873-46-0; $(PCy_3)_2W(CO)_3$, 73690-56-9; $(PCy_3)_2W(CO)_3(H_2)$, 104198-75-6; $(PCy_3)_2W(CO)_3(N_2)$, 73690-57-0; $(PCy_3)_2W(CO)_3(CH_3CN)$, 100995-29-7; $(PCy_3)_2W(CO)_3(py)$, 100995-31-1; $(PCy_3)_2W(CO)_3[P(OMe)_3]$, 100995-38-8; $(PCy_3)_2W(CO)_4$, 38800-78-1; $(C_7H_8)Cr(CO)_3$, 12125-72-3; $(C_{10}H_8)Cr(CO)_3$, 12110-37-1.

η^2-(N,C)-Pyridine and μ-$\eta^2(1,2)$:$\eta^2(4,5)$-Benzene Complexes of $(silox)_3Ta$ (silox = t-Bu_3SiO^-)

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Received February 5, 1988

The unusual capability of transition metals to coordinate to π-systems of organic molecules is recognized as playing a historic and important role in the growth of organometallic chemistry. This development is manifested in the widespread usage of aromatic hydrocarbons, such as cyclopentadienyl anion and arenes, as ancillary ligands bound with maximum hapticity to various metals.[1] Less common, but inherently interesting, are modes of binding which disturb the aromaticity of the fragment, yet fall short of utilizing the hydrocarbon's full complement of π-electrons.[1-7] Presented herein are pyridine (η^2)[7] and benzene $\{\mu$-$\eta^2(1,2)$:$\eta^2(4,5)\}$ adducts of $(silox)_3Ta$ (**1**, silox = t-Bu_3SiO^-)[8] which exhibit intriguing coordination geometries.

Treatment of pale blue **1** with pyridine, 1.0 equiv or an excess, resulted in the formation of an orange solution from which amber crystals of $(silox)_3Ta\{\eta^2$-(N,C)-$NC_5H_5\}$ (**2**) could be isolated in 65% yield (Figure 1). ^1H and ^{13}C NMR spectra of **2** revealed 5 inequivalent ring positions, including a broad singlet at δ 3.89 and corresponding α-carbon resonance at δ 81.96. Table I lists the spectral assignments of **2** as determined via comparisons with the free ligand,[9] decoupling, HETCOR, and labeling studies. An X-ray structural investigation of the complex[10] fully established the η^2 coordination mode of the pyridine.[7,11,12] The skeletal view

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[†] On leave from the Central Research Institute of Chemistry, Hungarian Academy of Science, Budapest, Hungary.

[‡] Alfred P. Sloan Foundation Fellow (1987–1989).

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(10) Crystal data for $(silox)_3Ta\{\eta^2$-(N,C)-$NC_5H_5\}$ (**2**): orthorhombic, *Pbca*, λ(Cu Kα), $\mu = 51.87$ cm^{-1}, $a = 22.378$ (12) Å, $b = 32.582$ (13) Å, $c = 13.162$ (4) Å, $T = 25$ °C, $Z = 8$, $V = 9596.2$ (72) $Å^3$, $R = 0.051$, $R_w = 0.075$, 5340 (82.5%) reflections where $|F_o| \geq 1.5\sigma(F_o)$. Other angles: N–C1–C2, 120.4 (11)°; C1–C2–C3, 118.6 (12)°; C2–C3–C4, 124.8 (12)°; C3–C4–C5, 119.8 (13)°; C4–C5–N, 112.5 (11)°; Ta–C5–N, 69.1 (6)°; Ta–N–C5, 70.2 (6)°; C5–Ta–N 40.7 (5)°; C5–Ta–O1,O2,O3, 117.4 (4), 119.5 (5), 93.4 (4)°; N–Ta–O1,O2,O3, 101.9 (4), 96.8 (3), 133.6 (3)°. Esd's for the $(silox)_3Ta$ core: Ta–O, 0.006 Å; Si–O, 0.007 Å; ∠Ta–O–Si, 0.4°.

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