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Pendent group effects, PGEs, in P-donor ligands

By

Anthony J. Poë

Lash Miller Chemical Laboratories

University of Toronto, Toronto, Canada M5S 3H6

Table S1 Analysis of C-O stretching frequencies in $Ni(CO)_3L$	χ(exptl.)	pKa	Θ	χ(calc.)
L	8.55	**8.65**	118	7.095963
	10.6	**6.5**	122	9.763847
PMe3	6.3	**8.69**	132	6.091295
PPhMe2	5.4	**8.64**	132	6.159651
PEt3	5.25	**8.43**	132	6.446746
P(n-Pr)3	9.3	**6.25**	136	9.155643
P(n-Bu)3	11.3	**4.9**	140	10.72983
PPhEt2	5.7	**7.97**	143	6.329205
PPh2Et	13.25	**2.73**	145	13.3572
P(i-Bu)3	11.3	**3.84**	145	11.8397
PPh3	10.5	**4.57**	145	10.8417
P(p-Meϕ)3	16.8	**1.03**	145	15.68131
P(p-MeOϕ)3	15.7	**1.97**	145	14.39621
P(p-Clϕ)3	5.25	**8.65**	145	5.263851
P(p-Fϕ)3	1.4	**9.7**	170	2.131976
p(p-Me2Nϕ)3	0	**11.4**	182	-1.0064
PCy3				
P(t-Bu)3				

These data were used to provide the material for Table 2

Table S2: **$Fe(CO)_4L$ data: L = PX_3**

X3	0.012χ(exp)	5.7pKa	θ	0.012χ(est)	Δ	π(p)	
Me3	0.0984	49.4	118	0.082546	0.015		
Et3	0.0696	49.6	132	0.066157	0.0034		
n-Bu3	0.0516	48.1	132	0.067655	-0.016		
t-Bu3	0	65.1	182	-0.00714	0.0074		
Ph3	0.06	15.6	145	0.085075	-0.025		
p-F3	0.084	7.94	145	0.092724	-0.0087		
p-CF3	0.132	-7.94	145	0.108581	0.0234		Δ/π(p)
OMe3	0.24	14.8	107	0.082546	0.157	2.8	0.056
OEt3	0.211	18.9	109	0.066157	0.145	2.9	0.05
(OPh)3	0.274	-11.5	128	0.067655	0.206	4.1	0.052

-0.00116	-0.001	0.268324
0.000438	0.000323	0.062903
0.820717	0.021361	#N/A
9.15554	4	#N/A
0.008356	0.001825	#N/A

Units of 0.012χ(exp) etc. are kJ/mol

Table S3 Analysis of C-O stretching frequencies in $Co(NO)(CO)_2L$ (kJ mol^{-1} units)

L	$100 \times \chi$exptl $\times 0.0124$	5.7p*K*a	θ	πp	χ(est.) all Ls	χ(est.) "non πs"
			132			
PEt3	11.16	49.53	132	0	9.960647	10.35463
PBu3	11.16	48.05	170	0	10.44012	10.8345
PCy3	4.96	49.53	145	0	5.765778	5.109458
PPh3	18.6	15.56	140	0	19.53065	19.57451
PPh2Et	18.6	27.36	145	0	16.25982	16.43868
PpMeOPh	18.6	21.9	136	0	17.47672	17.51885
PPhEt2	11.06	35.63	101	0	14.0222	14.30938
mtpb	47.12	9.92	107	5	46.46502	27.47655
P(Ome)3	33.48	14.82	109	2.8	35.30525	25.05961
P(Obu)3	33.48	18.87	128	2.7	33.36741	23.4704
P(Oph)3	47.12	-11.4		4.1	46.74639	30.66242

Table S4 Data for oxidation potentials for Cp(CO)LFe(COMe) in units of kJ mol^{-1}

L	E0(exptl) kJmol-1	χd/kJmol-1	Ear	πp	Eo(est) kJmol-1	Δ	Δ/πp	E0(est) kJmol-1 ALL Ls
Me3	34.644	0.1026	0	0	34.27202			34.41806
Et3	38.021	0.0756	0	0	37.53192			37.51526
iPr3	42.364	0.0414	0	0	41.66111			41.43838
Bu3	38.504	0.063	0	0	39.0532			38.96062
iBu3	38.021	0.0684	0	0	38.40122			38.34118
Cy3	44.294	0.0168	0	0	44.63124			44.26027
Ph3	24.222	0.159	3	0	23.79759			23.73966
p-MeO	28.13	0.126	3	0	27.7819			27.52513
p-Me	26.895	0.138	3	0	26.33306			26.14859
p-F	19.947	0.1884	3	0	20.24793			20.36715
p-Cl	17.92	0.2016	3	0	18.6542			18.85297
p-CF3	13.182	0.246	3	0	13.29349			13.75979
Ph2Me	25.959	0.1512	2	0	25.96096			26.0373
Ph2Et	27.696	0.1332	2	0	28.13422			28.1021
Ph2Pr	27.985	0.1344	2	0	27.98934			27.96445
Ph2iPr	30.494	0.1152	2	0	30.30748			30.16691
Ph2Bu	27.792	0.1356	2	0	27.84446			27.8268
Ph2Cy	31.264	0.1092	2	0	31.03191			30.85517
PhMe2	30.591	0.126	1	0	30.22516			30.33092
PhEt2	33.003	0.1032	1	0	32.97795			32.94633
PhBu2	33.679	0.1032	1	0	32.97795			32.94633

PhCy2	36.188	0.0642	1	0	37.68669			37.42007
OMe3	11.966	0.2112	0	2.8	21.16002	-9.19	-3.28	12.96235
OEt3	14.958	0.1956	0	2.9	23.04351	-8.09	-2.79	14.43049
OiPr3	18.046	0.1584	0	2.9	27.53491	-9.49	-3.27	18.69774
OiBu3	14.379	0.186	0	3	24.20258	-3.82	-3.27	15.21035
OC..Cl3	6.755	0.246	0	3.6	16.95838	-10.2	-2.83	6.399526
etpb	4.0337	0.24	0	5	17.6828	-13.7	-2.73	2.588756
OpMeO3	1.534	0.27	0	3.8	14.0607	-12.5	-3.3	3.003738
OpCl3	-0.6176	0.3264	0	4	7.251144	-7.87	-1.97	-4.10869
OpMe	0.8685	0.2688	0	4.1	14.20558	-13.3	-3.25	2.177312
P(Oph)3	-0.9071	0.2832	0	4.1	12.46697	-13.4	-3.27	0.525472
						Av=-3.02±0.13		
Alkyl and	aryl ligands only						(sans 1.97)	
-1.22163	-120.737	46.65961	#N/A	#N/A		ALL LIGANDS		
0.18742	4.170139	0.318854	#N/A	#N/A	-3.2136	-1.4029	-114.711	46.18742
0.995302	0.554699	#N/A	#N/A	#N/A	0.315056	0.287611	5.840892	0.50107
2012.685	19	#N/A	#N/A	#N/A	0.99464	1.022931	#N/A	#N/A
1238.568	5.84612	#N/A	#N/A	#N/A	1732.094	28	#N/A	#N/A
					5437.327	29.29887	#N/A	#N/A

Table S5 Data for hν(σ→σ*) for Mn2(CO)8L2

L	hν/kJ/mol	5.7pKa'	θ - 130	Ear	hν(est)	Δ	100Δπ	Eox	100Δπ
PEt3	337	45.41	2	0	335.4277	1.6	0	0	0
P-n-Bu3	337	49.46	2	0	335.9224	1.1	0	0	0
PPhEt2	329	33.89	3	1	330.5832	-1.6	0	0	0
P-i-Bu3	333	47.7	6	0	334.588	-1.6	0	0	0
p-CF3*	316.4	-7.93	13	3	316.3615	0	0	0	0
p-Cl*	318.1	4.96	15	3	317.3764	0.7	0	0	0
PPh3	319	18.71	15	3	319.0559	-1	0	0	0
p-Me*	319	25.45	15	3	319.8792	-0.9	0	0	0
p-MeO*	321.5	29.27	15	3	320.3458	1.2	0	0	0
PPh2Et	324	26.24	10	2	324.5324	-0.5	0	0	0
PPh2Cy	321.5	31.95	23	2	321.5918	-0.1	0	0	0
P-i-Pr3	329.5	56.37	30	0	328.9306	0.6	0	0	0
PPhCy2	324	47.35	32	1	324.1117	-0.1	0	0	0
PCy3	326.8	64.24	40	0	327.0934	-0.3	0	0	0
P(Ome)3	342	4.74	0	0	*331*	11	9.6	3	9.6
Pf(Ome)2	337	8.44	0	1	*328.3*	8.7	5.2	2	5.2
Pf2(Ome)	329	11.92	2	2	*325*	4	2.5	1	2.5
P(Oph)3	338	-15.92	0	0	*328.5*	9.5	11	3	11
P(O-i-Pr)3	349.7	19.28	0	0	*332.8*	16.9	7.8	3	7.8

* P(p-XC6H4)3

Table S5
(cont)

c	b	α	e	**Δ vs. Eox and 100ΔπΔ**	**& 100Δπ**	for eqn (3)
-3.15741	-0.27985	0.122151	330.4405	10.6154	-1.98931	0.91177
0.504827	0.030662	0.035897	1.746342	1.914087	0.570391	1.19212
0.980284	1.095894	#N/A	#N/A	0.964236	1.424502	#N/A
165.7383	10	#N/A	#N/A	40.44126	3	#N/A
597.1473	12.00984	#N/A	#N/A	164.1274	6.087621	#N/A

Table S6 Data for IP analysis

L	IP/kJ/mol	c(d)/kj/mol	Ear	IP(est)	πp	Δ	Δ/n
PMe3	833	0.106	0	829.2616	0		
PMe2Ph	809	0.131	1	809.3409	0		
PMePh2	798	0.156	2	789.4201	0		
PEt3	804	0.0781	0	804.5445	0		
PBu3	781	0.0651	0	793.0276	0		
PPhBu2	775	0.098	1	780.1056	0		
P-i-Pr3	777	0.0428	0	773.2716	0		
PCy3	748	0.0174	0	750.7693	0		
P-t-Bu3	744	0	0	735.3543	0		
PPh3	758	0.164	3	754.4387	0		
p-Me2N	666	0.0651	3	666.8214	0		
p-MeO	722	0.13	3	724.3175	0		
p-Me	733	0.143	3	735.8344	0		
p-F	784	0.195	3	781.9021	0		
p-Cl	789	0.208	3	793.4191	0		
p-F3C	835	0.254	3	834.1713	0		
Etpb	960	0.25	0	956.8338	5	3.17	1.06
P(Ome)3	883	0.222	0	932.0281	2.8	-49	-16.3
P(Oet)3	865	0.196	0	908.9942	2.9	-44	-14.7
P(Oph)3	849	0.293	0	994.9283	4.1	-146	-48.7
P(O-i-Pr)3	845	0.166	0	882.4167	2.9	-37.4	-12.5
PMe2Cl	888	0.244	0	951.5183	1.6	-63.4	63.4
PMeCl2	951	0.383	0	1074.661	3.5	-124	-62

PCl3	1033	0.521	0	1196.918	5.3	-164	-54.7
PPhCl2	936	0.402	1	1049.425	3.5	-155	-56.5
PPh2Cl	844	0.283	2	901.9316	1.8	-142	-58
P-t-BuCl2	897	0.347	0	1042.768	3.5	-146	-73

-42.0687	885.9179	735.3543	#N/A	Av. Of Cl-
1.550391	31.10416	2.770756	#N/A	containing
0.985546	5.591398	#N/A	#N/A	ligands=
443.2063	13	#N/A	#N/A	61.3±2.7
27712.57	406.4286	#N/A	#N/A	