Optically Active Transition Metal Compounds, 116[◇]

Bond Lengths Co–C(CO), Co–N(NO) and Angles L–Co–C(CO), L–Co–N(NO) in Tetrahedral Complexes[☆]

Henri Brunner*, **Josef Breu**, and **Peter Faustmann**

Institut für Anorganische Chemie der Universität,
D-93040 Regensburg, Germany
Fax: (internat.) +49(0)941/9434439
E-mail: henri.brunner@chemie.uni-regensburg.de

Received June 22, 1998

Keywords: Cobalt complexes / Carbonyl complexes / Nitrosyl complexes

The bond lengths Co–C(CO), Co–N(NO) and angles L–Co–C(CO), L–Co–N(NO) in six tetrahedral complexes, determined by X-ray crystallography, were analysed and compared with the calculated compound $Co(CO)_2(NO)PH_3$. Distinct differences were found which allow a differentiation of the two similar ligands CO and NO. These differences are used to assign CO and NO ligands in cases where this has not been possible before including a structure in which the two independent molecules in the unit cell are diastereomers. The relationship seems to hold not only for tetrahedral compounds but also for other polyhedral coordination types.

Introduction

In an extensive review Tolman determined the steric demand, i.e. the cone angles, of a huge number of ligands exept the linear two-atom ligands CO and NO.[2] In many reports on X-ray structure analyses it was stated that the CO and NO groups could not be distinguished due to their similar size, for example, in complexes of the type $Co(CO)(NO)L_2$.[3][4] The structure of $Co(CO)_3(NO)$ was determined by gas-phase electron diffraction.[5] During our investigations on optically active carbonyl(nitrosyl)cobalt complexes[6][7] we realised that there might be a distinct difference between the ligands CO and NO, which could be used for future assignments.

Ab initio Molecular Structures

Covalent and nonbonding intramolecular interactions determine the shape of the molecular potential energy hypersurface. However, geometries as observed in the solid state result from the interplay of intra- and intermolecular interactions. For flexible organometallic species molecular structure and crystal packing influence each other in a complex manner.[8]

To improve the reliability of the experimentally observed molecular structure parameters and to exclude the possibility of molecular structures being determined by intermolecular interactions we optimised the gas phase structure of $Co(CO)_2(NO)PH_3$ employing the density functional code DMOL[9] We used "DNP" basis sets[10] with inner cores frozen, a "FINE" integration grid, and the Vosko, Wilk, Nusair parametrization[11] of the exchange correlation energy in the homogeneous electron gas. The local approximation was applied in SCF iterations and the final LDA density was used for nonlocal corrections of both energy and gradients using the functions proposed by Perdew and Wang[12] and Becke[13] for correlation and exchange, respectively. The geometries were fully optimised without any symmetry constraints employing a mode following Newton-Raphson technique and the BFGS updating scheme for the Hessian.[14]

To check the agreement the molecular structures were minimised starting with coordinates taken from two different crystal structure determinations, SAPFIY = $[Co(CO)_2(NO)]_2(C_{31}H_{35}N_2O_2P_3)$[15] and GEHCIF = $Co(CO)_2(NO)(C_{16}H_{13}N_2O_2P)]$[16] and with P-ligands adjusted to PH_3. Finally, C and N atoms of the GEHCIF structure were exchanged (GEHCIF*) and the structure minimised starting from this "wrong" assignment. There is a good agreement between the results of these calculations with both the experimental gas phase structure[5] and the DFT minimised structure[17] of $Co(CO)_3(NO)$ (Table 1). However, as already noticed in ref.[17] the computed metal−C and metal−N distances are too short and the errors in the bond lengths are larger as for pure carbonyl compounds.[18]

All three minimisations converge to nearly identical geometries. The Co−C(CO) distance is 1.77 Å and the Co−N(NO) distance is 0.12 Å shorter, a difference that is larger than bond length errors of XRD structure determinations. This difference has been used before to assign carbonyl and nitrosyl groups in M(CO)(NO) fragments.[19][20] The most remarkable result, however, is the difference be-

---

[◇] Part 115: Ref.[1].

1434−1948/98/1212−1871 $ 17.50+.50/0

Table 1. Experimental and ab initio gas-phase geometries (in Å and degrees) of carbonyl(nitrosyl)cobalt complexes

Parameter	SAPFIY[15]	GEHCIF[16]	GEHCIF*	$Co(CO)_3(NO)$, DFT[17]	$Co(CO)_3(NO)$, Exp.[5]
R_{Co-N}	1.651	1.649	1.650	1.665	1.671
R_{Co-C}	1.768	1.767	1.767	1.810	1.843
	1.767	1.768	1.770		
R_{N-O}	1.178	1.177	1.177	1.178	1.180
R_{C-O}	1.162	1.162	1.162	1.163	1.136
	1.162	1.162	1.162		
R_{Co-P}	2.172	2.175	2.170	–	–
$\alpha_{(N)-Co-(C)}$	118.3	117.2	114.8	114.7	107.7
	117.5	115.9	118.9		
$\alpha_{(C)-Co-(C)}$	103.5	103.7	103.5	103.9	111.2
$\alpha_{(C)-Co-(PH3)}$	101.7	102.9	102.1	–	–
	99.5	101.0	101.3		
$\alpha_{(N)-Co-(PH3)}$	113.6	114.1	114.0	–	–

tween the P–Co–C(CO) and the P–Co–N(NO) angles which has not been documented before. The latter is more than ten degrees larger than the former. The values found are 113.6–114.1° for the P–Co–N(NO) angles and 99.5–102.9° for the P–Co–C(CO) angles. Given these pronounced differences in structural parameters, it should be possible to unequivocally assign NO and CO groups in XRD structure determinations.

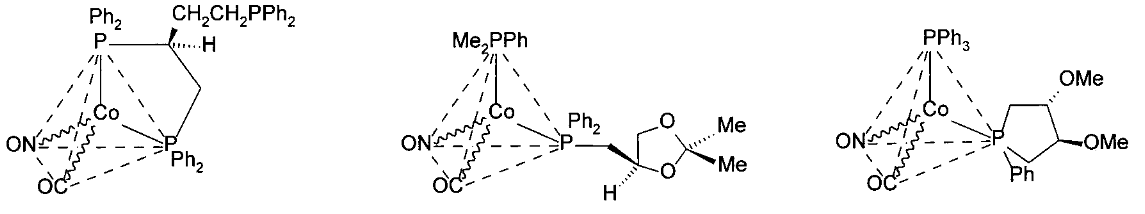
Crystal Structure Analyses

Crystal structure refinements were carried out for the six carbonyl(nitrosyl)cobalt complexes shown in Figure 1.

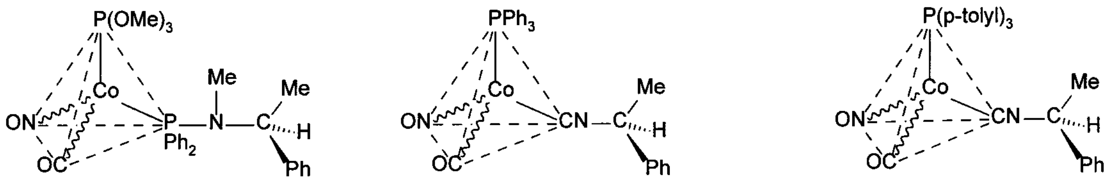
Details of the structure determinations and the crystal structure parameters were previously published.[6][7] However, for the present study all the structures were refined again in a consistent manner applying the SHELX-97 program package.[21] SHELXL refines against F^2 and all data were used in the full-matrix least-squares method. We also avoided any restraints, except for complex **5** for which DELU restraints were applied to remedy for the small reflex/parameter ratio. For compound **4** a new and larger data set was collected. Methyl H atoms were placed in idealised positions based on difference electron synthesis and torsion angles were refined with fixed isotropic displacement parameters of $1.5U_{eq}$ (parent C). All other H atoms were placed in idealised positions and refined with fixed isotropic displacement parameters of $1.2U_{eq}$ (parent C). All other atoms were refined anisotropically. The weighting scheme recommended by the program was used and refinement was continued until complete convergence (maximum shift/esd < 0.001) was achieved. It should be noted that the smaller isotropic temperature factor of nitrogen than that of carbon has been used previously for nitrosyl/carbonyl differentiation.[19][20]

For each complex two refinements were carried out. These differ only in the SFAC number used at the sites of the carbon atom of the CO group and the nitrogen atom of

Figure 1. Tetrahedral carbonyl(nitrosyl)cobalt complexes for which a structure refinement was carried out



1 Co(CO)(NO)(1,2,4-triphos) **2** Co(CO)(NO)(PMe_2Ph)(glyphos) **3** Co(CO)(NO)(PPh_3)(phenyl-tarpholan)



4 Co(CO)(NO)[$P(OMe)_3$](PN*) **5** Co(CO)(NO)(PPh_3)[CNCH(Me)(Ph)] **6** Co(CO)(NO)[P(p-tolyl)$_3$][CNCH(Me)(Ph)]

Table 2. Number of reflections and R indices of the refined structures

Complex	Total number of reflections	Number of unique reflections	Number of obsd. reflections with $I > 2\sigma_I$	L.S. parameters	$R1$[b] (all data)	$wR2$[c]) (all data)	$GooF$[d] (all data)	Flack parameter x
1	6801	6801	4489	433	0.0974	0.1141	1.033	0.0668 (0.02)
1 [a]					0.0998	0.1223	1.034	0.0728 (0.02)
2	5611	5579	4985	320	0.0430	0.0843	1.039	−0.0126 (0.01)
2 [a]					0.0439	0.0882	1.040	−0.0110 (0.01)
3	3865	2717	2027	354	0.0893	0.1025	1.089	0.0031 (0.03)
3 [a]					0.0903	0.1047	1.091	0.0017 (0.03)
4	12342	4667	4284	337	0.0281	0.0596	0.983	−0.0086 (0.01)
4 [a]					0.0305	0.0680	0.985	−0.0063 (0.01)
5	1949	1762	936	306	0.1612	0.2069	1.016	−0.0080 (0.07)
5 [a]					0.1620	0.2095	1.013	−0.0030 (0.07)
6	8477	8477	5943	680	0.0760	0.1294	1.124	0.0015 (0.02)
6 [a]					0.0766	0.1316	1.121	0.0051 (0.02)

[a] Values after exchanging the SFAC cards at the position of the carbon atom of the CO group and the nitrogen atom of the NO group. The number of reflections remains unchanged. – [b] $R1 = \Sigma||F_0|-|F_C||/\Sigma|F_0|$. – [c] $wR2 = \{\Sigma[w(F_0^2 - F_C^2)^2]/\Sigma[w(F_0^2)^2]\}^{1/2}$. – [d] $GooF = S = \{\Sigma [w(F_0^2 - F_C^2)^2]/(n\text{-}p)\}^{1/2}$ with n = number of reflections, p = total number of parameters refined, and $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$ with $P = [2F_C^2 + \mathrm{Max}(F_0^2,0)]/3$.

the NO group. In Table 2 the resulting refinement parameters are listed.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101715. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code +44(1223)336−033; E-mail: deposit@ccdc.cam.ac.uk].

Carbonyl and nitrosyl groups were initially assigned according to the observed bond length differences. For all six complexes the correct configuration gives slightly smaller values for the R indices. However, the differences for the two possible configurations at the cobalt atom are by no means significant and would not allow a conclusive assignment of NO and CO groups. The configuration space is large enough to allow good agreement between observed and calculated structure factors even for the wrong configurations. As expected, neither are meaningful differences displayed in the Flack parameters. Whereas R indices are rather insensitive, wrong assignment is clearly documented in the displacement parameters (Table 3).

Both ligands CO and NO bind to the same metal centre and are expected to have very similar displacement parameters. For the correct cobalt configuration the parameters of the nitrogen atom of the NO group and of the carbon atom of the CO group are indeed of the same magnitude. After exchange of the SFAC numbers of these two atoms, the parameters at the C site become larger and those at the N site become smaller. U_{eq} parameters at the C site (calculated as a nitrogen atom) are up to three times larger than those at the position N (calculated as a carbon atom). This is illustrated for two representative examples in Figure 2 (only the central cobalt coordination sphere is shown).

In a preceding paper we were not able to determine the absolute configuration of the complexes **2** and **4**.[7] With the results presented here we are able to do so. The investigated crystal of complex **2** is assigned the configuration (S_{Co},S_C), while for complex **4** the configuration can unambiguously be determined as (R_{Co},S_C).

An even more spectacular result was obtained for complex **6**. In complex **6** two independent molecules are arranged in a pseudo-centrosymmetric way in the unit cell; only the methyl group at the asymmetric C atom disturbs the inversion symmetry. We first assumed the same configuration for both cobalt atoms. During the present study we realised that this was not correct. In fact the two molecules seem to have different configurations. In other words the unit cell contains the two diastereomeric complexes that differ only in the configuration at the cobalt centre. Molecule A has a (R_{Co},S_C) and molecule B (S_{Co},S_C) configuration. This explains the fact that we were not able to separate the diastereomers of **6**, whereas in all other cases at least enriched samples could be obtained by fractional crystallization.[7]

The bond distances Co−C(CO) and Co−N(NO) of complexes **1**−**6** are listed in Table 4. For the correct configuration the values are in line with expected values. They range from 1.703 to 1.749 Å for the Co−C(CO) distance and

Table 3. Anisotropic, equivalent, and main axis displacement parameters for C and N of the CO and NO groups

Complex	Label[b]	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}	U_1	U_2	U_3	U_3/U_1
1	N(1)	0.048(3)	0.043(2)	0.036(2)	−0.003(2)	−0.002(2)	−0.008(2)	0.0423(14)	0.0329	0.0402	0.0539	1.64
	C(41)	0.039(3)	0.042(3)	0.035(3)	−0.004(2)	0.001(2)	0.007(2)	0.0387(17)	0.0306	0.0372	0.0482	1.57
1 [a]	N(1)	0.031(2)	0.027(2)	0.019(2)	−0.0067(19)	−0.004(2)	−0.009(2)	0.0257(12)	0.0116	0.0271	0.0383	3.29
	C(41)	0.074(4)	0.063(3)	0.052(3)	−0.003(3)	0.007(3)	0.006(3)	0.0630(19)	0.0484	0.0628	0.0778	1.61
2	N(1)	0.0374(13)	0.0553(15)	0.0402(13)	0.0137(11)	0.0053(10)	−0.0038(12)	0.0443(8)	0.0277	0.0418	0.0634	2.29
	C(33)	0.0524(17)	0.0350(13)	0.0406(14)	0.0033(13)	−0.0049(13)	−0.0053(13)	0.0427(9)	0.0330	0.0391	0.0560	1.70
2 [a]	N(1)	0.0259(12)	0.0404(14)	0.0301(13)	0.0106(11)	0.0047(9)	−0.0024(11)	0.0321(8)	0.0193	0.0301	0.0470	2.44
	C(33)	0.0671(19)	0.0527(16)	0.0525(16)	0.0035(15)	−0.0051(15)	−0.0073(16)	0.0574(10)	0.0488	0.0514	0.0720	1.48
3	N(1)	0.068(6)	0.064(5)	0.067(6)	−0.002(4)	0.017(5)	0.026(5)	0.069(3)	0.0502	0.0631	0.0950	1.89
	C(31)	0.054(6)	0.054(6)	0.046(5)	0.010(5)	0.004(4)	0.022(5)	0.054(3)	0.0390	0.0554	0.0662	1.70
3 [a]	N(1)	0.044(5)	0.048(5)	0.046(5)	−0.003(4)	0.016(4)	0.023(5)	0.046(3)	0.0247	0.0476	0.0657	2.66
	C(31)	0.075(6)	0.098(8)	0.062(6)	0.013(5)	0.007(5)	0.037(6)	0.081(4)	0.0568	0.0776	0.1089	1.92
4	N(1)	0.0279(12)	0.0221(10)	0.0329(10)	0.0069(8)	−0.0027(10)	0.0043(9)	0.0276(6)	0.0165	0.0301	0.0364	2.20
	C(22)	0.0217(13)	0.0203(11)	0.0336(13)	0.0064(9)	0.0044(10)	0.0015(10)	0.0252(7)	0.0177	0.0204	0.0375	2.12
4 [a]	N(1)	0.0153(12)	0.0120(10)	0.0188(10)	0.0054(8)	−0.0010(10)	0.0060(10)	0.0154(6)	0.0056	0.0179	0.0226	4.07
	C(22)	0.0334(15)	0.0384(14)	0.0476(15)	0.0089(11)	0.0053(12)	−0.0015(12)	0.0398(8)	0.0289	0.0368	0.0537	1.86
5	N(1)	0.050(11)	0.097(13)	0.103(14)	−0.030(11)	−0.009(10)	0.023(10)	0.089(7)	0.0476	0.0813	0.1394	2.93
	C(28)	0.038(12)	0.069(15)	0.15(2)	0.002(15)	−0.026(13)	0.014(11)	0.091(9)	0.0322	0.0816	0.1602	4.98
5 [a]	N(1)	0.026(10)	0.076(13)	0.070(13)	−0.023(11)	0.005(10)	0.014(9)	0.062(7)	0.0250	0.0503	0.1120	4.48
	C(28)	0.051(12)	0.102(17)	0.20(3)	−0.019(17)	−0.027(14)	0.020(11)	0.126(12)	0.0456	0.1267	0.2051	4.50
6 A	N(2)	0.034(3)	0.058(3)	0.107(5)	−0.016(3)	−0.007(3)	−0.018(3)	0.067(2)	0.0333	0.0610	0.1075	3.22
	C(31)	0.047(3)	0.066(4)	0.048(3)	−0.028(3)	−0.004(3)	−0.018(3)	0.0537(19)	0.0324	0.0472	0.0814	2.52
6 A [a]	N(2)	0.030(3)	0.045(3)	0.084(4)	−0.011(3)	−0.008(3)	−0.016(2)	0.0531(19)	0.0288	0.0463	0.0844	2.93
	C(31)	0.051(3)	0.084(4)	0.067(4)	−0.036(3)	−0.003(3)	−0.021(3)	0.068(2)	0.0459	0.0531	0.1038	2.26
6 B	N(4)	0.069(4)	0.056(4)	0.089(4)	−0.004(3)	−0.031(3)	−0.020(3)	0.073(2)	0.0482	0.0679	0.1032	2.14
	C(71)	0.062(4)	0.088(5)	0.050(4)	−0.033(3)	−0.010(4)	−0.017(4)	0.069(3)	0.0343	0.0589	0.1150	3.35
6 B [a]	N(4)	0.049(4)	0.045(3)	0.066(4)	−0.002(3)	−0.018(3)	−0.018(3)	0.054(2)	0.0395	0.0516	0.0721	1.83
	C(71)	0.086(5)	0.109(5)	0.067(4)	−0.044(4)	−0.019(3)	−0.017(4)	0.092(3)	0.0424	0.0765	0.1569	3.70

[a] See explanation in Table 2. – [b] See refs.[6][7] for labeling scheme.

from 1.643 to 1.702 Å for the Co–N(NO) distance. Only complex **5** does not fit into this picture. This might be because the number of measured reflections is too small relative to the number of parameters for a reliable refinement. After exchanging the carbon and nitrogen atom in **5** the distances remain rather constant for each site.

A conclusive assignment could also be based on the P–Co–N(NO) and P–Co–C(CO) angles as listed in Table

Figure 2. Platon plots of the core of the complexes **1** (left) and **4** (right). After exchanging the SFAC cards for the carbon and nitrogen atoms the anisotropic displacements parameters differ strongly (bottom)

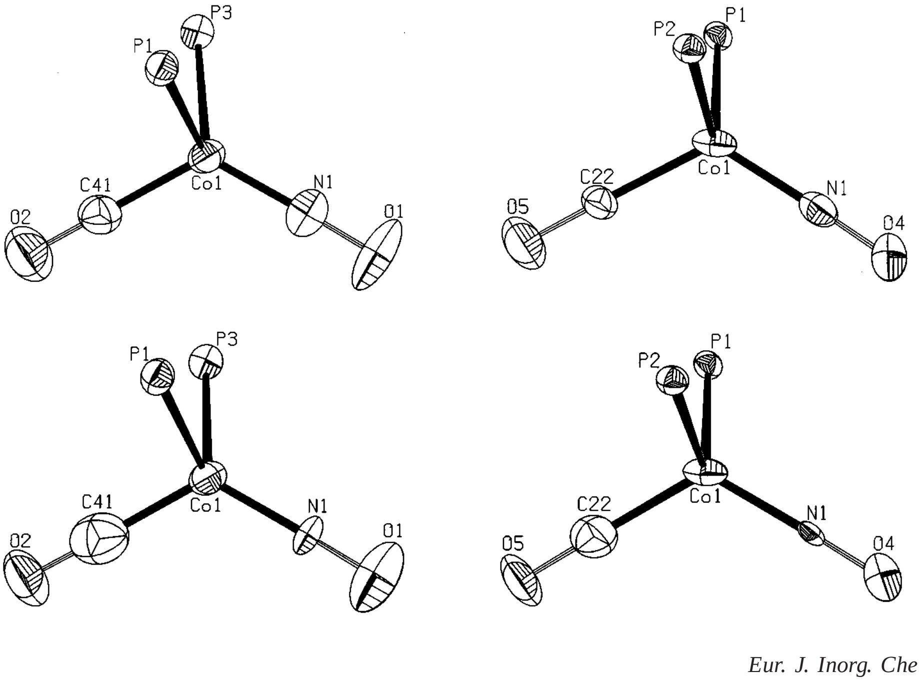


Table 4. Bond lengths in Å around the cobalt center

Complex	Co–C(CO)	C–O	Co–N(NO)	N–O	Co–L1 [b]	Co–L2 [b]
1	1.752(5)	1.157(7)	1.645(4)	1.174(6)	2.2087(17)	2.1953(18)
1 [a]	1.640(4)	1.162(6)	1.763(6)	1.169(8)	2.2090(17)	2.1960(18)
2	1.713(3)	1.156(4)	1.686(2)	1.171(3)	2.2136(13)	2.2069(13)
2 [a]	1.688(2)	1.161(4)	1.716(3)	1.164(4)	2.2131(13)	2.2071(13)
3	1.711(11)	1.151(13)	1.643(11)	1.183(15)	2.208(2)	2.204(3)
3 [a]	1.616(11)	1.170(15)	1.736(12)	1.162(14)	2.207(2)	2.203(3)
4	1.749(2)	1.146(3)	1.669(2)	1.177(3)	2.1498(6)	2.2073(6)
4 [a]	1.667(2)	1.170(3)	1.756(2)	1.143(3)	2.1499(7)	2.2073(6)
5	1.60(3)	1.24(4)	1.70(2)	1.16(3)	2.225(6)	1.93(3)
5 [a]	1.66(2)	1.14(3)	1.63(3)	1.27(4)	2.225(6)	1.91(3)
6 A	1.716(8)	1.163(10)	1.683(8)	1.149(12)	2.2087(19)	1.862(9)
6 A [a]	1.683(8)	1.138(12)	1.721(6)	1.164(9)	2.208(2)	1.863(9)
6 B	1.704(8)	1.152(10)	1.700(9)	1.171(13)	2.209(2)	1.865(9)
6 B [a]	1.678(9)	1.188(13)	1.698(8)	1.163(10)	2.210(2)	1.859(9)

[a] See explanation in Table 2. – [b] L1, L2: the ligands other than CO or NO. L1 has higher priority than L2.

Table 5. Bond angels in degrees around the cobalt center

Complex	L1–Co–N(NO)	L1–Co–C(CO)	L2–Co–N(NO)	L2–Co–C(CO)	C–Co–N	L1–Co–L2
1	118.82(14)	104.40(18)	119.83(15)	97.43(14)	121.5(2)	88.38(4)
1 [a]	104.69(18)	118.64(14)	97.4(2)	119.80(15)	121.5(2)	88.38(5)
2	112.94(9)	105.79(10)	110.37(9)	101.54(10)	123.43(14)	99.72(2)
2 [a]	105.83(10)	112.87(10)	101.56(10)	110.48(9)	123.34(14)	99.74(3)
3	115.9(3)	101.7(3)	109.2(3)	104.0(4)	122.3(5)	101.33(9)
3 [a]	101.8(3)	115.5(3)	104.0(4)	109.5(3)	122.2(5)	101.33(9)
4	109.35(7)	104.55(9)	115.96(7)	100.94(8)	120.82(10)	103.33(2)
4 [a]	104.51(9)	109.40(9)	100.89(9)	115.90(9)	120.89(11)	103.34(2)
5	109.9(7)	106.1(9)	110.7(9)	108.2(11)	119.6(12)	100.6(8)
5 [a]	106.1(9)	109.7(7)	107.9(11)	111.1(9)	119.5(12)	100.9(8)
6 A	108.0(2)	101.7(3)	113.5(3)	108.5(4)	123.5(4)	97.9(2)
6 A [a]	101.7(3)	108.8(2)	108.3(3)	113.6(3)	122.9(4)	97.9(2)
6 B	107.1(2)	105.4(3)	112.3(4)	111.9(5)	121.6(5)	94.6(2)
6 B [a]	105.7(3)	106.6(3)	112.4(4)	112.2(4)	121.4(5)	94.5 (2)

[a] See explanation in Table 2.

5. As expected from the gas-phase structures for complex **1** P–Co–N(NO) angles are 22° and 14° larger than the corresponding P–Co–C(CO) angles. For the other complexes this difference is about 5 to 10°. These results indicate that the nitrosyl group has a larger steric demand than the carbonyl group.

To further back these conclusions a statistical analysis has been carried out on other carbonyl-nitrosyl complexes registered in the Cambridge Structural Database. We found 41 octahedral complexes and 18 trigonal-bipyramidal or tetrahedral complexes (in addition to the six cobalt complexes discussed above). The octahedral complexes contain 95 M(CO)(NO)P groups and the other complexes another 31 such groups. We did not try to assess the quality of the deposited structural data nor did we check on what basis the authors assigned the nitrosyl and carbonyl groups. This would be difficult and unreliable without the original data sets at hand. However, at a first glance the data confirm the results of the present study. We compared the values of P–M–C(CO) and P–M–N(NO) angles. In 41 cases the latter angle is more than 5° larger than the former. In another 42 cases the difference is between 1° and 5°, still with the P–M–N(NO) angle being the larger one. A small difference of less than ±1° is found for 19 pairs. Only in 24 cases the P–M–C(CO) angle is found to be more than 1° larger than the P–M–N(NO) angle.

☆ Dedicated to Professor *Edgar Niecke* on the occasion of his 60th birthday.

[1] H. Brunner, T. Neuhierl, B. Nuber, *J. Organomet. Chem.* **1998**, *563*, 173.
[2] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313.
[3] V. G. Albano, P. L. Bellon, G. Ciani, *J. Organomet. Chem.* **1972**, *38*, 155.
[4] J. T. Lin, S. Y. Wang, Y. C. Chou, M. L. Gong, Y.-M. Shiow, H.-M. Gau, Y. S. Wen, *J. Organomet. Chem.* **1996**, *508*, 183.
[5] K. Hedberg, L. Hedberg, K. Hagen, R. R. Ryan, L.H. Jones, *Inorg. Chem.* **1985**, *24*, 2771.
[6] H. Brunner, P. Faustmann, A. Dietl, B. Nuber, *J. Organomet. Chem.* **1997**, *542*, 255.
[7] H. Brunner, P. Faustmann, B. Nuber, *J. Organomet. Chem.* **1998**, *556*, 129.
[8] D. Braga , F. Grepioni, *J. Chem. Soc., Chem. Commun.* **1996**, 571.
[9] DMOL, MSI, 9658 Scranton Road, San Diego, CA 92121-2777, USA.
[10] B. Delley, *J. Chem. Phys.* **1990**, *92*, 508.
[11] S. H. Vosko, L. Wilk, M. Nusair, Can. *J. Phys.* **1980**, *58*, 1200.
[12] J. P. Perdew, Y. Wang, *Phys. Rev.* **1992, B45,** 13244.
[13] A. D. Becke, J. *Chem. Phys.* **1988**, *88*, 2547.
[14] A. Banerjee, N. Adams, J. Simons, R. Shepard, J. Phys. Chem., **1985**, *89*, 52.

[15] J. Ellermann, N. Will, F. Knoch, *J. Organomet. Chem.* **1989**, *366*, 197.
[16] J. Ellermann, E. Kock, H. Zimmermann, M. Gomm, *J. Organomet. Chem.* **1988**, *345*, 167.
[17] F. Bohr, H. Chermette, M. F. Ruiz-Lopez, *Int. J. Quantum Chem.* **1994**, *52*, 1039.
[18] L. Fan, T. Ziegler, *J. Chem. Phys.* **1991**, *95*, 7401.
[19] J. W. Faller, K. H. Chao, H. H. Murray, *Organometallics* **1984**, *3*, 1231.
[20] U. Eberhardt, G. Mattern, G. Schiller, *Chem. Ber.* **1988**, *121*, 1525.
[21] G. Sheldrick, University of Göttingen, **1997**.

[I98194]