Oxygen-17 Nuclear Magnetic Resonance Spectra of Mononuclear Manganese and Dinuclear Group 6 Metal Carbonyl Complexes

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Oxygen-17 n.m.r. spectra have been measured for two series of metal carbonyl derivatives, $[MnR(CO)_5]$ (R = H, CH_3, and Br) and $[MM'(CO)_{10}]^{n-}$ (n = 0 for M = M' = Mn; n = 1 for M = Mn, M' = Cr, Mo, and W; n = 2 for M = M' = Cr, Mo, and W), at natural ^{17}O abundance. Oxygen-17 chemical shifts for mononuclear $[MnR(CO)_5]$ are explained in terms of substituent electronegativity which would be expected to increase the paramagnetic shielding as the charge density at the oxygen 2*p* orbitals decreases. For the dinuclear metal carbonyls, the diamagnetic shielding effect due to the metal–metal bond appears to be responsible for a subtle change in ^{17}O resonance frequencies.

WHEREAS the first report on ^{17}O n.m.r. spectra of metal carbonyls by Bramley *et al.*[1] appeared as early as 1962, it was not until the last few years that ^{17}O n.m.r. spectroscopy proved instrur in elucidating structural and bonding problems tal carbonyl derivatives. In the intervening deca(nain problems seemed to be due to two inherent difficulties in observing ^{17}O n.m.r. resonances: a low natural abundance (0.037%) and line-broadening due to an electric quadrupole moment ($I = \frac{5}{2}$) of the ^{17}O nucleus. We have recently demonstrated that ^{17}O n.m.r. spectra of various tungsten carbonyl derivatives are easily obtained at the naturally abundant ^{17}O level with the aid of the Fourier-transform n.m.r. technique and that ^{17}O n.m.r. chemical shifts serve as a sensitive measure of the σ-donor : π-acceptor ratio of the ligands in some $[WL(CO)_5]$-type compounds.[2a] Similar empirical treatment of carbonyl ^{17}O chemical shifts was made by Todd and co-workers[2b-e] for a variety of metal carbonyl derivatives and they found a 'metal triad effect' (see below) on the ^{17}O chemical shift of a series of Group 6 and 7 metal carbonyl compounds.

A recent upsurge of ^{17}O n.m.r. studies on metal carbonyls[2,3] prompted us to examine systematically the effects of various factors such as formal electron charge at the metal atom on ^{17}O chemical shifts and to interpret them with the aid of information from some molecular orbital (m.o.) calculations. In this paper we select two series of compounds, $[MnR(CO)_5]$ (R = H, CH_3, Cl, and Br) for which *ab initio* m.o. calculations have been reported[4] and isoelectronic $[MM'(CO)_{10}]^{n-}$ ($n = 0$ for M = M' = Mn; $n = 1$ for M = Mn, M' = Cr, Mo, and W; $n = 2$ for M = M' = Cr, Mo, and W), to increase our knowledge of ^{17}O n.m.r. chemical shifts for metal carbonyl derivatives.

EXPERIMENTAL

Materials.—$[MnH(CO)_5]$ (1), $[Mn(CH_3)(CO)_5]$ (2), and $[MnBr(CO)_5]$ (3) were prepared by the literature methods.[5] $[MnCl(CO)_5]$ (4) was obtained as follows: $[Mn_2(CO)_{10}]$ (0.5 g) was dissolved in CCl_4 (50 cm^3) and photolysed for 30 min with a Riko 100-W high-pressure mercury lamp under an argon atmosphere. The solvent was vacuum-stripped and the resulting yellow solid was sublimed at 50 °C/0.1 mmHg † to give 0.45 g of (4). $[Mn_2(CO)_{10}]$ (5), purchased from the Strem Chemical Co., was purified by sublimation. Dinuclear $[NEt_4][MnCr(CO)_{10}]$ (6), $[NEt_4][MnMo(CO)_{10}]$ (7), $[NEt_4][MnW(CO)_{10}]$ (8), $[NEt_4]_2[Cr_2(CO)_{10}]$ (9), $[NEt_4]_2[Mo_2(CO)_{10}]$ (10), and $[NEt_4]_2[W_2(CO)_{10}]$ (11) were synthesized according to the literature methods.[6,7] The samples of $[Cr(CO)_6]$ (12), $[Mo(CO)_6]$ (13), and $[W(CO)_6]$ (14) were used as received. Sample solutions for ^{17}O n.m.r. measurements were prepared under a nitrogen atmosphere by dissolving each 200—300 mg sample in 2 cm^3 of a solvent which was distilled under a nitrogen atmosphere just prior to use.

Oxygen-17 N.M.R. Measurements.—Fourier-transform ^{17}O n.m.r. spectra were recorded for samples in natural abundance (0.037%) on a Varian FT-80A spectrometer operating at 10.782 MHz and externally locked on a deuteriated water signal. The spectra of (10) and (11) were recorded at 0 °C, while the others were obtained at room temperature using a 10-mm (outside diameter) sample tube. Transients (*ca.* 5×10^5) were accumulated with a 90° pulse and an acquisition time of 0.02 s. For an 8 000-Hz spectral width, 323 data points were available in the time-domain spectra by keeping the Fourier number at 16 384. Chemical shifts were measured as frequency shifts from synthesizer frequency (8.532 MHz) and were expressed in parts per million in the sense that a positive chemical shift denotes a resonance to a lower field than that of water oxygen which resonated at 10.783 17 MHz.

RESULTS

Spectral Results, Assignments, and Trend in Chemical Shifts.—Most of the metal carbonyl compounds employed in this study showed reasonably sharp ^{17}O n.m.r. signals and, therefore, there was no problem in the measurement at the natural abundance level. The limited solubility of $[MnCl(CO)_5]$ in typical solvents and facile dimerization to $[\{MnCl(CO)_4\}_2]$ frustrated our repeated attempts to obtain a good ^{17}O n.m.r. spectrum of this compound.[3] The chemical-shift data are collected in Table 1 and typical ^{17}O n.m.r. spectra are shown in Figure 1.

The mononuclear complexes (1), (2), and (3) exhibited two peaks with relative intensity 1 : 4. The weak peak is assigned to the axial and the strong peak to the equa-

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† Throughout this paper: 1 mmHg = (101 325/760) N m^{-2}; 1 dyn = 10^{-5} N.

TABLE 1

Oxygen-17 n.m.r. chemical shifts and relevant force-constant data

Compound	$\delta(^{17}O)$/p.p.m.[a] equatorial	$\delta(^{17}O)$/p.p.m.[a] axial	k(M–M)/ mdyn Å^{-1}	k(CO)/mdyn Å^{-1} equatorial	k(CO)/mdyn Å^{-1} axial
(1) $[MnH(CO)_5]$ [b]	382	376			
(2) $[Mn(CH_3)(CO)_5]$ [b]	381	372			
(4) $[MnCl(CO)_5]$	378.7	386.7 [c]			
(3) $[MnBr(CO)_5]$ [d]	386	392			
(5) $[Mn_2(CO)_{10}]$ [e]	387	367	0.59 [f]	16.33	16.06 [g]
(6) $[NEt_4][MnCr(CO)_{10}]$ [e]	398 [h] 375 [i]		0.50 [j]	15.89 [h] 15.14 [i]	15.21 [h] 14.27 [i,j]
(7) $[NEt_4][MnMo(CO)_{10}]$ [e]	400 [h] 368 [k]		0.60 [j]	15.83 [h] 15.31 [k]	15.15 [h] 14.34 [i,k]
(8) $[NEt_4][MnW(CO)_{10}]$ [e]	393 [h] 358 [l]		0.71 [j]	15.91 [h] 15.14 [l]	15.24 [h] 14.23 [j,l]
(9) $[NEt_4]_2[Cr_2(CO)_{10}]$ [e]	367	382	0.60 [m]	14.70	12.00 [n]
(10) $[NEt_4]_2[Mo_2(CO)_{10}]$ [e]	390	365	0.68 [m]	15.30	13.10 [n]
(11) $[NEt_4]_2[W_2(CO)_{10}]$ [e]	380	342	0.73 [m]	15.30	13.10 [n]
(12) $[Cr(CO)_6]$ [e]	376				
(13) $[Mo(CO)_6]$ [e]	367				
(14) $[W(CO)_6]$ [e]	357				

[a] Chemical shifts from $H_2{}^{17}O$. [b] In toluene. [c] From ref. 3. [d] In CH_2Cl_2. [e] In nitromethane. Solvent effects are less than 1 p.p.m. for the Mn carbonyl derivatives. [f] C. O. Quicksall and T. G. Spiro, *Inorg. Chem.*, 1969, **8**, 2363. [g] F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 1965, **4**, 1328. [h] $Mn(CO)_5$ unit. [i] $Cr(CO)_5$ unit. [j] J. R. Johnson, R. J. Ziegler, and W. M. Risen, jun., *Inorg. Chem.*, 1973, **12**, 2349. [k] $Mo(CO)_5$ unit. [l] $W(CO)_5$ unit. [m] From ref. 13. [n] S. Onaka, unpublished results.

torial carbonyls (*trans* and *cis* to H, CH_3, and Br, respectively). The homodinuclear complexes (5), (10), and (11) showed doublets with the low-field peak about four times as strong as the high-field one, while (9) displayed a weaker peak at lower field and a stronger peak at higher field with relative intensity 1 : 4. The weaker peaks are assigned to the axial carbonyls *trans* to the metal–metal bond. Their chemical shifts show the ' metal triad effect ' when (9), (10), and (11) are compared; the upfield shift accompanies increases in the nuclear size of the metal atoms from Cr to W.[2c] For heterodinuclear compounds (6), (7), and (8), only doublets with approximately equal intensities were detected. We failed to observe separate resonance frequencies of ^{17}O nuclei due to axial carbonyls. As it was difficult to obtain the spectra with better signal-to-noise ratio for these metal carbonyls, the question of whether the chemical shifts of the axial carbonyls overlap with those of the equatorial ones or if they are buried under the noise level somewhere else should be deferred until more reliable spectra are obtained with ^{17}O-enriched samples. As far as the observed doublets are concerned, the higher field resonances exhibit a characteristic upfield shift, namely, the ' metal triad effect ' on going from Cr to W. The chemical shifts of the lower field signal are rather indifferent to the change in the metal atoms. Therefore, we assign the resonances at lower field to the equatorial carbonyls of the $Mn(CO)_5$ moiety and those at higher field to the carbonyls co-ordinated to Group 6 metal atoms.

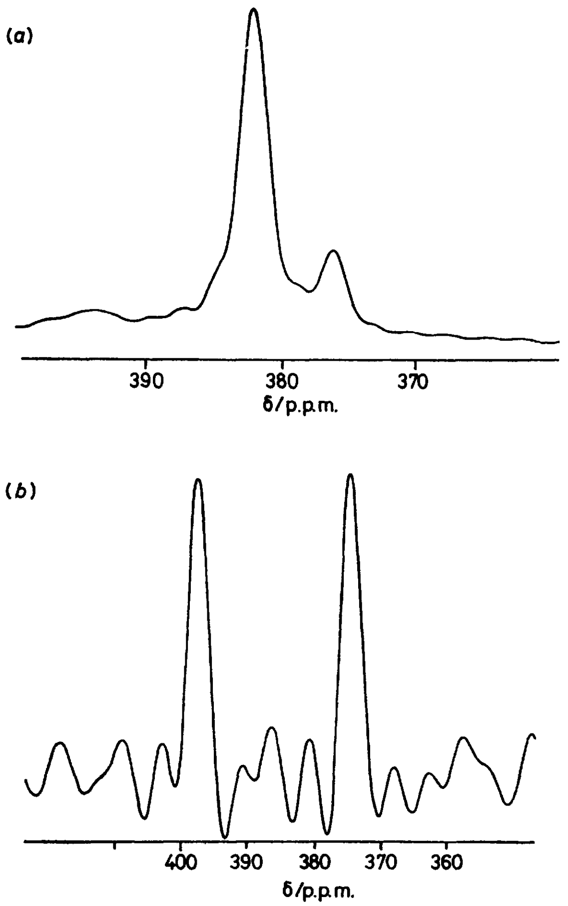

FIGURE 1 Oxygen-17 n.m.r. spectra (10.78 MHz) of (*a*) $[MnH(CO)_5]$ in toluene and (*b*) $[NEt_4][MnCr(CO)_{10}]$ in nitromethane

As is noted in Table 1, ^{17}O resonances of the axial carbonyls are shifted downfield by substituting a more electronegative group for group R in a series of $[MnR(CO)_5]$, whereas such substitution causes only small downfield shifts for the equatorial carbonyl groups. Internal shifts of the ^{17}O resonances between the axial and equatorial carbonyls are less than 10 p.p.m. For a series of homonuclear dimetal carbonyls, (9)—(11), the internal shift increases with the increase in the nuclear size and the maximum shift is as large as 38 p.p.m. for (11). In heterodimetal carbonyls, (6)—(8), ^{17}O chemical-shift values due to the carbonyls co-ordinated to Group 6 metal atoms are close to those of the parent hexacarbonyls (12)—(14), respectively. The signals due to the $Mn(CO)_5$ unit are somewhat shifted downfield as compared with that of the parent $[Mn_2(CO)_{10}]$. In a brief summary of the trends, the ^{17}O chemical-shift values of $[MM'(CO)_{10}]^{n-}$ are plotted against those of mononuclear $[M(CO)_6]$ in Figure 2.

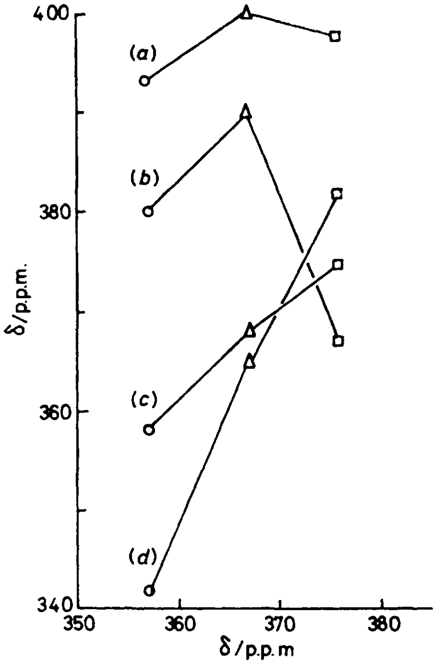

FIGURE 2 Plots of ^{17}O n.m.r. chemical shifts due to $[MM'(CO)_{10}]^{n-}$ *versus* those of $[M(CO)_6]$: (*a*) $[(\mathit{O}C)_5MnM(CO)_5]^-$, (*b*) $[(ax\text{-}CO)(eq\text{-}C\mathit{O})_4MM(eq\text{-}C\mathit{O})_4(ax\text{-}CO)]^{2-}$, (*c*) $[(OC)_5MnM(C\mathit{O})_5]^-$, and (*d*) $[(ax\text{-}C\mathit{O})(eq\text{-}CO)_4MM(ax\text{-}C\mathit{O})(eq\text{-}CO)_4]^{2-}$; (□) Cr, (△) Mo, and (○) W

DISCUSSION

Interpretation of ^{17}O *Chemical Shifts.*—Oxygen-17 n.m.r. chemical shifts are dominated by the local paramagnetic contribution to the total screening constant σ.[8,9] The paramagnetic screening σ_p is expressed by Pople[10] in the form of equation (1), where $\langle r_{2p}^{-3}\rangle$ is the mean inverse

$$\sigma_p = -(\text{constant})\ \langle r_{2p}^{-3}\rangle\langle\Delta E\rangle^{-1}\ (Q_A + \sum_{A \neq B} Q_{AB}) \quad (1)$$

cube of the radius of the oxygen $2p$ electrons, $\langle\Delta E\rangle$ is the average excitation energy of the low-lying oxygen $2p$ state, and the terms Q_A and Q_{AB} represent the imbalance of charge in the p-orbital of atom A and the bond order between atom A and the adjacent atoms B. Q_{AB} is nearly zero for singly bonded oxygen and increases as π-bonding strengthens. Inductive and mesomeric loss of a fraction of a p electron increases Q_A. Variation in the p-electron charge density affects the radial term similarly: loss of a fraction of a p electron from oxygen increases $\langle r_{2p}^{-3}\rangle$ a few percent. While we understand that these parameters are not fully independent variables, we are tempted to see which term may correlate to the experimentally found trends the best.

$[MnR(CO)_5]$.—Some data relevant to the above parameters are available from the *ab initio* calculations on $[MnR(CO)_5]$-type compounds performed by Guest *et al.*[4] In Table 2, the charge and orbital overlap populations of the carbonyl moieties are summarized.

The electron density at the axial carbonyl oxygen is in the order (2) > (1) > (4). The observed downfield shift is in parallel with the decrease in the calculated electron density which should lead to the increase in σ_p by increasing the Q_A term or contracting the oxygen $2p$ orbitals. Klemperer,[11] Kawada *et al.*,[2a] and Todd and co-workers[2c] have proposed that the trend of the ^{17}O shielding constants would be explained in terms of the π-accepting and/or σ-donating ability of ligand L opposite to the axial carbonyl. The π bond order between the carbon and oxygen atoms was considered to be dependent on L and contribute dominantly to σ_p of ^{17}O nuclei. When the π-accepting ability of L increases, σ_p should lead to a low-field shift. The calculated π bond order of the axial carbonyls is in the order (4) > (2) > (1). Although this trend is in accord with our knowledge on the π-accepting ability of the group R,[12] the observed order of the ^{17}O shielding constants of the axial carbonyls does not coincide with this π bond order. From the discussion advanced above, it seems conceivable that the electron density at the oxygen atoms is not determined by the π-accepting or donating ability of the R group alone, but the combined effect of the σ-donating and π-accepting abilities of the group R is responsible for the subtle change of electron density which governs the ^{17}O chemical shift.[2a] One important point we should be aware of here is that the electron-density argument is not always valid in the ^{17}O chemical shift. As given in Table 2, for example, the electron density of the equatorial carbonyls is more reduced than that of the axial carbonyl when an H or CH_3 group is replaced with Cl.[4] The oxygens in the equatorial carbonyls, however, resonate at a higher field in (3) and (4). Thus it seems reasonable to conclude that this kind of discussion is valid only for comparison of the ^{17}O chemical shifts of carbonyls in similar structural environments.

TABLE 2

Charges and bond overlap populations for oxygen orbitals of $[MnR(CO)_5]$ *

	Charge on oxygen atom		π Bond overlap population	
Compound	axial	equatorial	axial	equatorial
$[MnH(CO)_5]$	−0.34	−0.35	0.831	0.839
$[Mn(CH_3)(CO)_5]$	−0.35	−0.35	0.832	0.842
$[MnCl(CO)_5]$	−0.33	−0.32	0.848	0.859

* See ref. 4.

Reliable estimation of the $\langle\Delta E\rangle$ term in the equation of the local paramagnetic screening is not possible until the excitation energies of the oxygen $2p$ electrons are explicitly given. If we approximate the expected trend in $\langle\Delta E\rangle$ by that of the m.o. energy, we note that the m.o.s rich in the CO bonding tend to stabilize when H and/or a CH_3 group is substituted by Cl in $[MnR(CO)_5]$.[4] This should cause $\langle\Delta E\rangle$ to increase and thus σ_p will show an upfield shift of the ^{17}O resonances in (3) and (4), a trend which is opposite to the observed downfield shift. Thus the $\langle\Delta E\rangle$ term appears to play only a minor role in the ^{17}O shielding of the present series of $[MnR(CO)_5]$ compounds.

$[NEt_4][(OC)_5MnM(CO)_5]$ (M = Cr, Mo, *and* W).—When one $Mn(CO)_5$ moiety is replaced with anionic group $M(CO)_5^-$ in $[Mn_2(CO)_{10}]$, this gives the heterodinuclear metal carbonyls (6), (7), and (8) and such substitution causes ^{17}O resonances of the $Mn(CO)_5$ moiety to shift to downfield as compared with that of $[Mn_2(CO)_{10}]$. If the interpretation of ^{17}O chemical shifts for mononuclear $[MnR(CO)_5]$ given above is applied to the present series of compounds, the downfield shift suggests that the electron density of the oxygen atoms in the $Mn(CO)_5$ moiety would be decreased by this substitution. However, it is unlikely that the electron-withdrawing ability of the anionic $M(CO)_5^-$ moiety is stronger than that of the replaced $Mn(CO)_5$ group. Indeed, this latter supposition is substantiated by the comparison of the metal–metal and metal–carbonyl stretching force constants between isoelectronic $[CrMn(CO)_{10}]^-$ and $[Mn_2(CO)_{10}]$; k(Mn–Cr) is smaller than k(Mn–Mn)[13] and the values of k(CO) for the $Mn(CO)_5$ group of the heterodimetal complex are smaller than those of $[Mn_2(CO)_{10}]$ (see Table 1). The smaller carbonyl stretching force constants indicate the increased electron localization on the oxygen atoms and this should result in an upfield shift of ^{17}O resonances. The observed downfield shifts of the carbonyl oxygens in the $Mn(CO)_5$ moiety will be due to other factors than the simple electron-density argument (see below).

$[NEt_4]_2[M_2(CO)_{10}]$ (M = Cr, Mo, *and* W).—The compounds of this type are obtained formally from the corresponding complexes $[(OC)_5MnM(CO)_5]^-$ by replacing the $Mn(CO)_5$ group with $M(CO)_5^-$. Such substitution causes ^{17}O resonances of the equatorial carbonyls to shift downfield and those of axial carbonyls upfield for M = Mo and W. The reverse is true for M = Cr. The metal–metal stretching force constants are increased by the substitution,[13] while the carbonyl stretching force constants, especially those of axials, are considerably reduced. Both the equatorial and axial k(CO) values are higher for M = Mo and W than for M = Cr.

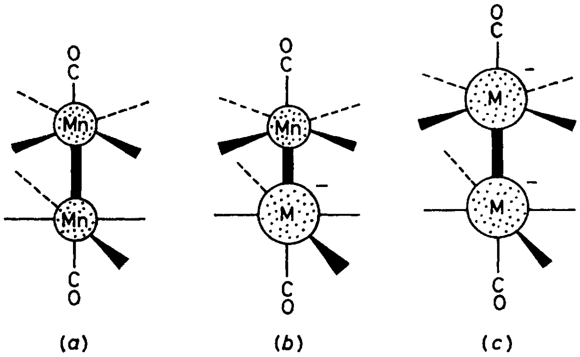

FIGURE 3 Schematic drawing of the electron distribution around the metal atoms in the dinuclear compounds (M = Cr, Mo, or W)

If the difference in these force constants in the series of homonuclear dimetal carbonyls is emphasized, it is evident that the electron density of the oxygen atoms may be reduced on descending Group 6 (Cr→W). This suggests a significant downfield shift of ^{17}O resonances as seen on going from the equatorial CO of Cr to those of Mo and W. The observed trend for the axial carbonyls is just the opposite to the one predicted by the electron-density argument. This anomaly and the discrepancy mentioned previously for the heterodinuclear metal carbonyls, namely, the observed high-field shift and the expected reduction in electron density of the CO oxygen in descending Group 6, are best interpreted in terms of the magnetic anisotropy of the metal–metal bond, a similar effect to the one reported by Cotton and co-workers[14] for explaining the large ^1H chemical-shift difference between the proximal and distal methyl groups in $[Mo_2(NMe_2)_6]$. Three models of typical electron distribution around each metal atom are given in Figure 3. If we adopt model (*a*) for the electron distribution around the manganese atoms of $[Mn_2(CO)_{10}]$, model (*b*) should be applicable to the heterodinuclear metal carbonyls (6)—(8), and model (*c*) to the homonuclear complexes (9)—(11). In model (*c*), diamagnetic shielding is more effective for the axial carbonyls than in models (*a*) and (*b*). Since the anisotropic effect should be enhanced with the increase of the nuclear size, the ^{17}O resonances due to the axial carbonyls will shift upfield on descending Group 6 in $[M_2(CO)_{10}]^{2-}$. As the equatorial carbonyls are situated in the opposite zone of the shielding cone made by the magnetic anisotropy of the metal–metal bond, the long-range shielding effect will induce a low-field shift for the equatorial carbonyls, a trend which is in parallel with the charge-density effect. The observed low-field shift in going from Cr to W is not monotonous and appears to indicate that the ^{17}O n.m.r. shielding is determined by the intricate balance between the local paramagnetic contribution due to the changes in charge density and the long-range diamagnetic anisotropy.*

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* A more detailed study may be necessary before we are fully able to make adequate comment on the anomalous chemical shift for the equatorial carbonyls of $[Cr_2(CO)_{10}]^{2-}$.

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